Environmental Life Cycle Assessment of Engineered Nanomaterials in Carbon Capture and Utilisation Processes

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Environmental Life Cycle Assessment of Engineered Nanomaterials in Carbon Capture and Utilisation Processes

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To Mam a'r Hen Ffŵl,

Mae hwn i chi, diolch am bopeth.

"Dyfal donc a dyr y garreg"

Welsh proverb ~ persistent strikes break the stone

Abstract

CO_2 is a waste product from a number of human activities such as fossil fuel power generation, industrial manufacturing processes, and transport. The rising concentration of CO_2 in the atmosphere is heating the planet's surface via the well-established greenhouse effect; a mechanism for many irreversible climate change impacts. Coupled to this is the ever-increasing global pressure over the availability and access to fossil fuel reserves; the foundations of modern society. In recognition of this CO_2 is gaining renewed interest as a carbon feedstock, a changing of attitude viewing it as an asset rather than waste. Carbon capture and utilisation (CCU) technologies are attempting to make use of it. However, little quantitative assessment work has been done to assess and verify such potentials.

This thesis applies the principles and framework of the life cycle assessment (LCA) - environmental management tool to early stage CO_2 utilisation laboratory processes. All processes employ engineered nanomaterials (ENM) to perform this function, a material class leading the way in the challenges of efficient and feasible CO_2 chemistry. The LCA contribution in this thesis acts as a measuring and a guiding tool for technology developers, in the first instance to document the cradle-to-gate impacts of a number of formed ENMs. Appreciating the net environmental benefits of ENM uptake within society has yet to be wholly established, and the unavailability of data is recognised as a major factor. The work of this thesis will thus contribute to knowledge gaps, and be informative to wider community seeking to quantify technical performance benefits of ENMs in the context of net life cycle impact burdens.

Finally the actual CCU processes are assessed, initially within the confines of the laboratory but further expanded for consideration at more industrially relevant scales. The potential for sound CCU performance were found achievable under best case conditions, with net GHG impact reductions over the life cycle, and the potential for lower impact carbon products, even carbon negative. However other environmental impacts such as ozone depletion, toxic emissions and the consumption of precious metal ores are impacts that require consideration in the use of such technologies.

Acknowledgments

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I was also privileged to be part of a wider consortium of researchers as part of the Grand Challenge Team, the content of this thesis is all founded on their work, especially that of Dr Daniela Plana and Professor David Fermin at the University of Bristol, and Dr Davide Mattia, Dr Rhodri Owen, Dr Justin O'Byrne and Dr Laura Murciano-Torrente from the University of Bath. Thank you all, this PhD is a testament to successful research collaboration in which you contributed so richly to towards.

Justin, you were a vital collaborator in this research but additionally you fulfilled the role of, friend, counsellor, conspirator and (dare I say it?) additional supervisor. We began this journey as strangers but continue as best friends. You're a great man.

Mam, Dad and Rhys. You've been three limitless pillars of support throughout everything in my life. I am so incredibly lucky to be part of such a loving family. I think this every day and in everything I do. Tadcu, wherever you are I hope you're proud.

Finally Áine, you weren't something I expected to find whilst researching a PhD but you're definitely the most important discovery. A force of nature and positive energy like no other! Your love, support, motivation, and perspective got me to the finishing line... I think we need a holiday now.

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Glossary: Abbreviations and Acronyms (AA)

CCS	**Carbon capture and storage**
CCU	**Carbon capture and utilisation**
CO_2	**Carbon dioxide**
CS	**Core-shell material**
CO_2 eq.	**Carbon dioxide equivalent emissions.**
CVD	**Chemical vapour deposition**
DECC	**Department of Energy and Climate Change**
DUKES	**Digest of United Kingdom Energy Statistics**
ENM	**Engineered nanomaterial, in alignment with other literature, synthetic materials/particles at the nanoscale.**
EPSRC	**Engineering and physical sciences research council**
F-T	**Fischer Tropsch**
GHG	**Greenhouse gas(es)**
GWP	**Global warming potential**
kWh	**Kilowatt-hour**
LCA	**Life cycle assessment**
LCI	**Life cycle inventory**
LCIA	**Life cycle impact assessment**
MWCNT	**Multi-walled carbon nanotubes**
Nano	**"The branch of technology that deals with dimensions and tolerances of less than 100 nanometres , especially the manipulation of individual atoms and molecules." (Oxford University Press 2008). Iso standards 27687:2008 and 11360:2010 give overviews and characterise the nanomaterials and particles to date (ISO 2008; ISO 2010),**
NM	**Nanomaterial(s): material with one or dimension less than 100nm1,**
NP	**Nanoparticle(s): two or more dimensions less than 100nm.**
NGC	**Nanotechnology Grand Challenge**
RWGS	**Reverse water-gas shift**

[1] Nanometer, nm, = 10^{-9} metres

sccm	**standard cubic centimetres per minute; gas flow rate measure at STP (see below).**
SiO_2	**Silica**
STP	**Standard temperature and pressure**
wt.	**Weight**

- SI prefixes are used throughout this thesis.
- All chemical substances are stated as their elemental symbols, e.g. Au being gold, and Pd palladium.
- Unless otherwise stated, all calculated values are for STP; 1 atm pressure, and 0°C.

Chapter 1: INTRODUCTION

"Too many leaders seem content to keep climate change at arm's length, and in its policy silo. Too few grasp the need to bring the threat to the centre of global security, economic and financial management. It is time to move beyond spending enormous sums addressing the damage, and to make the investments that will repay themselves many times over".

UN Secretary-General Ban Ki-moon, Remarks at the Council on Foreign Relations (February 2013)

Tackling global climate change and sustainable growth for all is seen by many as the greatest challenges of our time. The focus of scientists and technologists are aligning to address these challenges. Current technical barriers and uncertainties over potential solutions and their likely effectiveness are hampering much needed progress; areas in which this thesis endeavours to tread.

1.1 CO_2 CHALLENGE

CO_2 is a small molecule, its importance for the existence and sustained well-being of all biological occupants of this planet is absolute. The respiration of plants is dependent on CO_2 use as a photosynthesis input, from which the co-products of biomass and oxygen are made available to the rest of us eating and air-breathing folk. The global average temperature correlates directly to the measured concentrations of atmospheric CO_2 (Carr 2013), the pendulum swing between ice ages is in harmony with the abundance of this small molecule's presence (Fischer *et al.* 1999); indeed without it our planet would be plunged to -21 °C (Lacis *et al.* 2010).

Conversely, of late, too much CO_2 has resulted in increased greenhouse effects elevating average global temperatures. These changes are expected in the decades ahead to reach intolerable levels, beginning a series of environmental mechanisms that will drastically affect the climate, landscape, fatal to life for many humans and animals here on Earth. The International Panel on Climate Change (IPCC) have recently concluded that "*human influence on the climate system is clear*" (Stocker *et al.* 2013).

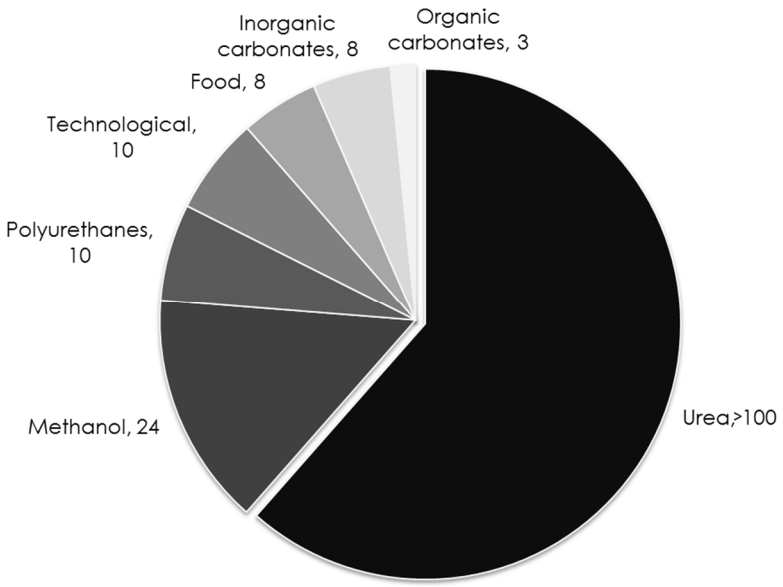

Figure 1-1 Different products formed from CO_2 [megatonnes/yr] (Metz *et al.* 2005)

Increased anthropometric activities since the industrial revolution namely, fossil fuel (FF) usage and rising population, has caused a sharp increase in CO_2 emissions. Despite CO_2 from natural origins represents the vast majority, 95.1 – 96.4%, of all current emissions, the biosphere has evolved a complex carbon cycle to successfully re-absorb these releases (Dixon *et al.* 1994; Janzen 2004)(IPCC). Indeed, nature is also sequestering approximately half of human CO_2 emissions. However, the unrecovered increment of CO_2 atmospheric concentration due to human activity is tipping the carbon cycle's scales. Mankind have been introducing ever more quantities of CO_2 into the atmosphere, but unlike nature, we're leaving it there; and at levels which current natural processes cannot deal with. This mounting up of CO_2 is the challenge we face, and if nature and our climatic system have each embraced CO_2 as an integral asset rather than a foe, isn't it time we began to do so as well?

"Oh small molecule

Friend or foe

To love or hate

To understand you better

Before it's too late!"

(Geoffrey A. Ozin)

CO_2 is viewed as waste by the majority of its emitters/producers. This should be addressed, especially given that for many decades established industries have had a

demand for it, either in its direct application or as a feedstock. CO_2 applications range in variety from the niche to established megatonne annual product scales, the largest of these are shown in Figure 1-1. Despite our mass usage of CO_2, it is but a fraction of what conservative estimates expect carbon capture to provide over the coming decades (IPCC), and an infinitesimal quantity compared to the net CO_2 flux entering the atmosphere due to human activity. Tapping into this abundant CO_2 is proving to be the challenge.

1.2 CARBON CAPTURE AND UTILISATION (CCU)

Mitigating measures are already underway in addressing the release of CO_2 into the atmosphere, including efforts to reduce primary fossil fuel (FF) usage through: use of renewables, more efficient infrastructure and technologies, and increased social awareness and change; realising the link between behaviour and emissions. Despite these efforts, even best case scenarios will see a steady net flux of CO_2 entering the atmosphere (Peters *et al.* 2013).

Grappling with inevitable CO_2 production from the many sources of FF combustion and major industries such as cement manufacture, has birthed interest in the carbon capture (CC) movement. Carbon capture technology fitted to point-source emitters is a technical solution with the theoretical potential to lower the net flux of anthropometric CO_2 release. Furthermore, atmospheric carbon capture offers the potential retrieval of atmospheric CO_2; limiting the damage caused by humanity to this point.

This thesis is concerned with carbon dioxide capture and utilisation[2] (CCU) technologies. The scope of which spans the capture of CO_2 from point-source emitters, e.g. power plants, or indeed the free atmosphere itself. Once captured CCU technologies subsequently transform CO_2 into societally useful products. Early research and development of CCU processes have already shown compatible products for sustainable fuels and feedstocks for many chemical industries including pharmaceuticals; the potential would overshadow the current usage of CO_2 shown in Figure 1-1 (Centi *et al.* 2011). CCU has the theoretic potential to elevate the importance of CO_2 in the technosphere, emulating its unrivalled status in the biosphere.

[2] *Utilisation* is used interchangeably in the literature with *conversion* and/or *recycling*, CCC or CCR respectively.

Despite the potential CCU has to offer, much uncertainty remains for the likely mitigating effects these technologies might provide. This thesis provides an evaluation for a number of emerging candidate CCU processes. Considering climate change mitigating impacts, and other wider environmental impact assessment damage criteria.

1.3 DRIVERS FOR CARBON CAPTURE AND UTILISATION; ROLE FOR LCA

Up to present day, the majority of the needs of the developed, and increasingly technologically developing nations of the world have been satisfied by the use of fossil fuels (FF) (IEA 2011a). They continue to provide the majority of our electricity sources, space heating, fuels for transportation (Christensen *et al.* 2008), and feedstocks to many industries, such as plastics, pharmaceuticals, dyes, tars, waxes.. The hydrogen economy remains at present a distant realisation (Ekins 2010), in both supply terms and enabling technologies (Rifkin 2003; Tseng *et al.* 2005). Current work for alternative sources of energy face issues, such as the uptake of solar renewables (Lewis and Nocera 2006), and bio-based fuels and products (Fernando *et al.* 2006; Hatti-Kaul *et al.* 2007). In addition to specific technical challenges, wider issues face the large scale deployment and integration into present infrastructure (Boyle 2004; Negro *et al.* 2012).

Therefore, to varying extents, our dependency on liquid hydrocarbons will remain as key parts of our lives, and the lives of future generations to come. Very radical societal changes would need to be witnessed - at least in the foreseeable term - before we cease to require the services provided by FF. However, in meeting society's demands, FF are facing a range of pressures, including (Armaroli and Balzani 2007; Chu and Majumdar 2012):

- Rising global population with evermore resource and energy demands,
- Concerns over reserves, and
- Political tensions arising for these previous issues, and wider factors.

Such pressures are likely to increase the interest and pursuit of alternatives. Amongst which is the use of CCU technologies, in order to supplement potential shortcomings of FF supply, and to act an intermediate stepping stone towards lower-carbon and hydrocarbon-free pathways (Song 2006; Centi and Perathoner 2009; Centi *et al.* 2011).

CCU technologies are a potential mitigating stop gap, or bridging technology, as we seek to advance from our dependency on FFs to more sustainable future pathways. Hydrocarbon fuels are a current necessity in modern society, especially for energy and transport activities. Environmental issues aside, our FF dependency is increasingly threatened by its decreasing stock availability, and vulnerability to political uncertainties. CCU offers the theoretical opportunity to de-couple hydrocarbon production from both geological and geo-political boundaries.

1.4 CCU VIA NANOTECHNOLOGY

Amongst the leading touted options available for CCU is the exploitation of nanotechnology (Roy *et al.* 2010; Centi *et al.* 2011; Taheri Najafabadi 2013), Nanomaterials are a class of materials with one of more dimension less than 100 nm (Oxford University Press 2008). Engineered nanomaterials (ENMs) are offering a plethora of potential environmentally beneficial applications, from reduced material consumption, enhanced energy efficiency, and performance boosting existing technical systems whilst offering the prospect of entirely new functions (Lines 2008). Specifically to the field of carbon dioxide conversion, the unique physiochemical properties of ENMs are leading technological breakthroughs required to make CCU a viable option (Peters *et al.* 2011; García-Martínez and Wang 2013).

Despite growing understanding of the potential applications in which ENMs could fulfil, very little quantitative environmental data for their integration in technology applications have been produced (Bauer *et al.* 2008; Hischier and Walser 2012a). This thesis provides quantitative measures for the synthesis impacts of several undocumented or data-lacking, ENMs and their precursors. The results of environmental life cycle assessments (LCA) are vital for the holistic assessment of technology solutions seeking to incorporating novel and emerging materials into their design (Hetherington *et al.* 2013), especially for environmental remediation processes such as CCU, but also for more far-ranging fields in which ENMs could be employed.

1.5 THESIS CONTRIBUTION

This thesis investigates emerging laboratory-synthesised materials and processes, which have demonstrated the ability to convert CO_2 into 'societally useful' carbon-based

compounds. These include alkanes and alkenes of chain lengths up to C7, methanol, formic acid and carbon monoxide. In specific cases other co-products such as process heat from exothermic reactions and the formation of hydrogen gas are obtained.

The LCA tool has been used to determine whether proposed CCU technology solutions are environmentally feasible pathways to pursue, considering; capture, use, and obtainable products. Answering key questions, such as whether processes achieve the goal of minimising CO_2 release to the environment, while producing products that are of a lesser environmental burden than existing industrial pathways. Although concerned with tackling a specific CO_2 mitigating challenge, carbon footprinting is not the only output of this work, but in parallel is the consideration of other environmental impacts that arise from the associated activities sourced from the use of candidate CCU technologies. Further to the immediate contribution in the assessment of early CCU technologies, this thesis has far-reaching implications, as highlighted in Figure 1-2, relevant to many other fields of research.

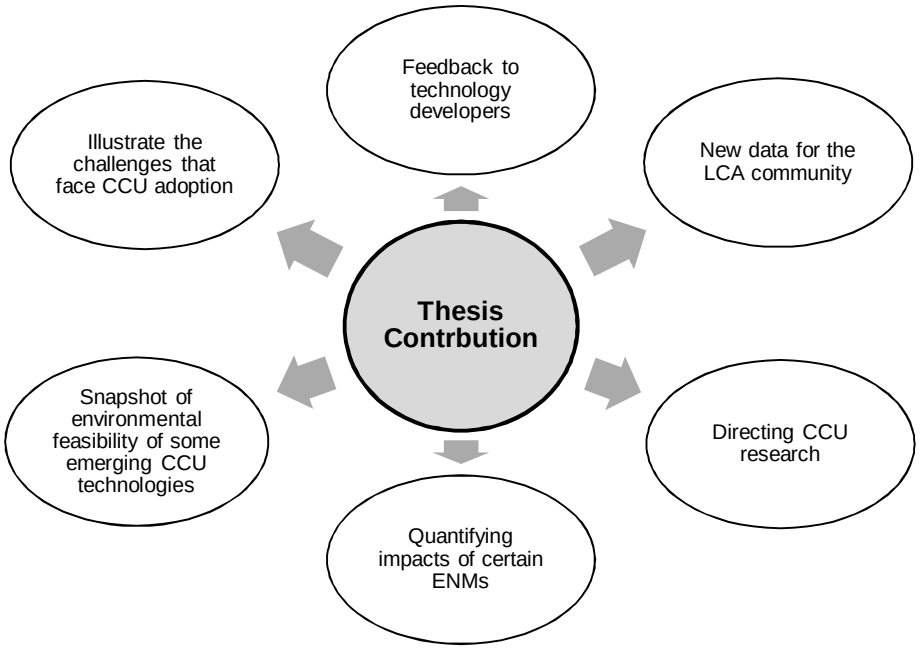

Figure 1-2 Thesis contribution

1.6 THESIS AIMS AND OBJECTIVES

The over-arching purpose of this thesis was to assess the environmental performance of a range of CCU technologies at the early stages of their development, drawing insight on their environmental impact and feasibility. In essence, the aim was to:

Aim: ***Provide a more quantitative understanding of the potential benefits, in terms of mitigating climate change and other environmental impacts, to guide those wishing to use nanotechnology solutions for the conversion of CO_2 into commodity products.***

In meeting this aim, five primary objectives were followed, each with their own set of sub-objectives and scopes:

Objective 1. Establish the environmental impacts of forming the nanomaterials

1.1. Cradle-to-gate of the formation routes of different materials; of use for the CCU application and wider research field.

1.2. Provide disaggregate data on all identifiable process flows involved in the production of ENMs.

1.3. Highlight the most dominant impacts for different production techniques.

1.4. Expansion of scope to cover end-of-life process activities, to either make materials 'benign' or retrieve embedded precious materials.

Objective 2. Establish the life cycle impacts of the developed CCU processes, and report on the environmental feasibility of further technology development

2.1. Construction of high detail laboratory setup inventory data.

2.2. Identify best materials and process operating conditions on a holistic basis, across the whole life cycle of the process(es).

2.3. Comparing processes assessed against existing/alternative functionally equivalent systems.

2.4. Forecasting of likely impacts inherent for all scales of technology development; adoption of a lean setup model. A model which:

- strips unnecessary laboratory process activities,
- reduce impacts from laboratory inefficiencies.

2.5. Setting of lifetime operational targets before life cycle benefits of an operating system are achieved; in order to become greenhouse gas (GHG), and other impact, neutral.

2.6. Utilisation of useful process co-products.

2.7. Environmental impacts and implications of resultant products formed.

Objective 3. Communicate to technology developers key life cycle results for action

3.1. Present accurate accounts of the factors behind the life cycle impacts of the operating process(es).

3.2. Highlight which factors are within the technology developer's control, and what life cycle activities are outside the boundaries of their process and material design and selection.

3.3. Demonstrate the effects of implementable process changes, detailing approach and assumptions so that the feasibility of such options can be further explored.

Objective 4. Communicate wider life cycle environmental impacts

4.1. In addition to potential greenhouse gas (GHG) damage, provide accounts of other life cycle impact effects on human health and the biosphere.

4.2. Appreciate process energy and material resource consumption.

4.3. Provide a characterised account of the nature and likely life cycle release points of formed ENMs.

1.7 THESIS CONTENT

The structure of the thesis is set out to answer the research aims in a coherent and progressing manner, introducing the field of work and present status, the conduct of specific case studies of ENM synthesis and CCU process operation, and presentation of major findings and discussion points.

1. Thesis Introduction
2. Background
3. Research Approach
4. LCA of forming Multi-Walled Carbon Nanotube and their preparation for CO_2 catalysis
5. LCA of Nano Iron and Palladium Catalyst Synthesis
6. Heterogeneous Conversion of CO_2 to Hydrocarbons via Reverse Water-Gas Shift and Fischer Tropsch Reactions
7. Aqueous electrochemical reduction of CO_2 using nano-catalyst electrode coatings
8. Key findings and discussion
9. Conclusions

Table 1-1 Where specific research questions and main thesis aims are addressed within the thesis

	Chapter						
	1	2	3	4	5	6	7
Introduction and overview of research conducted in this thesis							
Recognise the gaps in the field of ENM assessment, being mindful of these in the conducted studies							
Adopt a valid approach to account for CO_2 feedstock use throughout the life cycle							
Thesis objective 1							
Thesis objective 2							
Thesis objective 3							
Thesis objective 4							

1.8 ACKNOWLEDGING CONTRIBUTION TO THIS THESIS BY OTHERS

This research relied on the collaboration with researchers in the provision of direct and primary data sources for the assessments made. The author would like to acknowledge and explicitly thank the Nanotechnology Grand Challenge project team members whose work was the cornerstones to specific research avenues and chapters in this thesis, Electrochemical CO_2 reduction, Dr Daniela Plana, and other researchers working in Professor David Fermin's research group. Fischer-Tropsch coupled with the reverse water-gas shift reaction of CO_2 into hydrocarbons. Under the research teams of Dr Matthew Jones and Dr Davide Mattia, and the researchers Dr Rhodri Owen for nanometal-silica catalyst synthesis and testing, and Dr Justin O'Byrne concerned with the synthesis of multi-walled carbon nanotubes and its subsequent use as capable catalysts for CO_2 conversion. Dr Laura Murciano-Torrente for expertise in Aspen chemical engineering processing tool in the construction of an inventory dataset for ferrocene, a precursor for carbon nanotube synthesis. Finally, the Grand Challenge principal investigator, Prof Frank Marken for his oversight of the different collaborations. APPENDIX A: provides an oversight of the project team interaction.

1.9 DISSEMINATING THE RESEARCH

Journal Publications

- Lead author of "Identifying the largest environmental life cycle impacts during carbon nanotube synthesis via chemical vapour deposition." Journal of Cleaner Production (Griffiths *et al.* 2013a)

- Joint lead author "Using Life Cycle Assessment to Measure the Environmental Performance of Catalysts and Directing Research in the Conversion of CO_2 into Commodity Chemicals: a look at the potential for fuels from 'thin-air'." RSC Advances.(Griffiths *et al.* 2013b)

- Co-author "Use of LCA as a development tool within early research: challenges and issues across different sectors." The International Journal of Life Cycle Assessment(Hetherington *et al.* 2013)

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Conferences

- Great Western CO_2 Conference, University of Bath: June 2011; 'LCA work for the Grand Challenge Team', and June 2012; 'Life cycle thinking for CCU research'.

- 7th Conference on Sustainable Development of Energy, Water and Environmental Systems, SDEWES. Macedonia, 2012. 'LCA of environmental performance of iron based nanoscale catalysts for the conversion of CO_2 into fuels and chemical feedstocks'.

- SETAC 18th LCA Case Studies Symposium, Copenhagen, November 2012 'Addressing challenges faced in the LCA of nanomaterials: metal organic frameworks… and beyond!'.

Chapter 2: BACKGROUND

"You have to know the past to understand the present."
— Carl Sagan

Chapter Highlights

This chapter provides an overview of:

- LCA framework,
- Current challenges for LCA of ENMs.
- LCA suitability for new and emerging technology assessment,
- Life cycle drivers and application in carbon capture and utilisation assessments.

2.1 ENVIRONMENTAL LIFE CYCLE ASSESSMENT

In conducting technology environmental assessments, many tools exist for measuring the environmental impacts of different systems, amongst the most implemented are:

- Environmental Risk Assessment (ERA)

Environmental risk assessment is of importance when dealing with specific material and emission releases into the environment, providing a measure of the likely impacts that would arise from such a case.

- Carbon Footprint (CFP)

Greenhouse gas (GHG) accounting, or CFP, considers the climate change impacts of delivering a product or operating a system. The concern over global warming in recent years has meant carbon footprint, is at the forefront of policymakers minds when assessing the environmental effects mankind are having on the planet. GHG impact reporting has, arguably, been prioritised over all other environmental impacts, with CFP the most widely cited, and used environmental accounting metric, prevalent from household energy bills to consumer product labelling. GHG impacts are better characterised – as detailed in IPCC (2007b)- and measurements of different emitting technologies have been better quantified than any other substance release. Additionally, the nature of the forced-irradiative heating mechanism of GHG in the atmosphere is more readily interpreted and assessed than more localised toxicity impacts.

Primary energy is predominantly sourced from fossil fuels (IEA 2011b), and therefore energy use along the whole of a process life cycle closely relates to GHG impacts (Huijbregts *et al.* 2010). It is for this reasons that carbon and energy are often paired as the feedback most industrialists demand (Hammond and Jones 2008b). However, the use of CFP is not best representative of all impacts arising from a system (Laurent *et al.* 2012), appreciably not providing an insight into the extent finite resources are consumed, and specific toxicity impacts arising from a technology. CFP has been presented as a "springboard" (Laurent *et al.* 2012), raising awareness of environmental issues in policy and business practices, and leading on to more encompassing and holistic assessments as provided by LCA.

- Life Cycle Assessment (LCA)

LCA can be considered to follow the same framework as a complete carbon footprint assessment. However, LCA allows for a more comprehensive environmental assessment to occur, providing the best available predictions of the impact technologies have on the environment and human health. With specific consideration in the tools applicability in answering the objectives of this thesis, LCA affords insight into:

- Determining the whole life benefit of a system.
- Establishing whether the ENM in-use performance come at too great an environmental penalty
- CCU performance. Accounting for the avoided environmental impact, in the first instance from avoiding the direct release of CO_2 to the atmosphere, and subsequently the implications of producing carbon products via a CCU route.

2.1.1 *OVERVIEW OF LCA PROCESS*

LCAs origins come from the late 1960s (Guinée and Heijungs 2000), when it is widely accepted that the Coca Cola company were the first to implement a life cycle study, in deciding the merits of different containers for their famous drink (Baumann and Tillman 2004). At the time the company was most likely attempting to determine the implications of energy, material usage and working practices on the whole life costs of their products. However, the link between environmental improvement and cost-saving are long established (Porter and Van der Linde 1995), and considering as wide a scope as possible allows the greatest appreciation of the factors, and the greatest opportunity for process change and improvement (Klassen and McLaughlin 1996).

In essence, LCA is founded upon establishing the interaction a system (or group of systems) has with the environment. Establishing what resources are consumed, and what emissions and wastes are generated, ultimately detailing the extent in which an assessed system may affect or damage the natural world. The system's coverage is absolute. A full LCA measures all intrinsic activities involved, spanning primary raw material extractions, the use, up to the final disposal or re-use activities included within the assessment.

LCA has many strengths. Predominantly, it is considered as the only assessment tool which provides a quantitative measure of damage being caused due to the existence of system. Expanding further, a tool which can predict the *potential* impacts that a proposed system might likely cause. LCA is necessary to determine if applications being devised to remedy anthropometric environmental damage actually meet this objective. For example in CCU, when tackling GHG release mitigation, to assess the measurable knock on effects this has on other resource, and environmental issues.

Since the early 1990s the processes for implementing LCAs have been better coordinated amongst the scientific community, with arguably the Society of Environmental Toxicology and Chemistry (SETAC) driving the method into being a better defined and implementable form (Klopffer 2006); the involvement of the international standards organisation (ISO) occurred shortly after. In 2006 the, still current, ISO standards for the LCA process were released, an amalgamation of previous standards, they present the framework and guiding principle of a holistic life cycle approach for measuring the environmental impacts of a product or system. ISO 14040:2006 essentially provides an overview and the main "principles and framework" of LCA (ISO 2006a), whilst ISO 14044:2006 is a more detailed LCA standard, specifying the "requirements and guidelines" of the LCA methodology (ISO 2006b). LCA follows a series of sequential steps spanning the initial stakeholder engagement, technology assessment and the presentation of environmental implications.

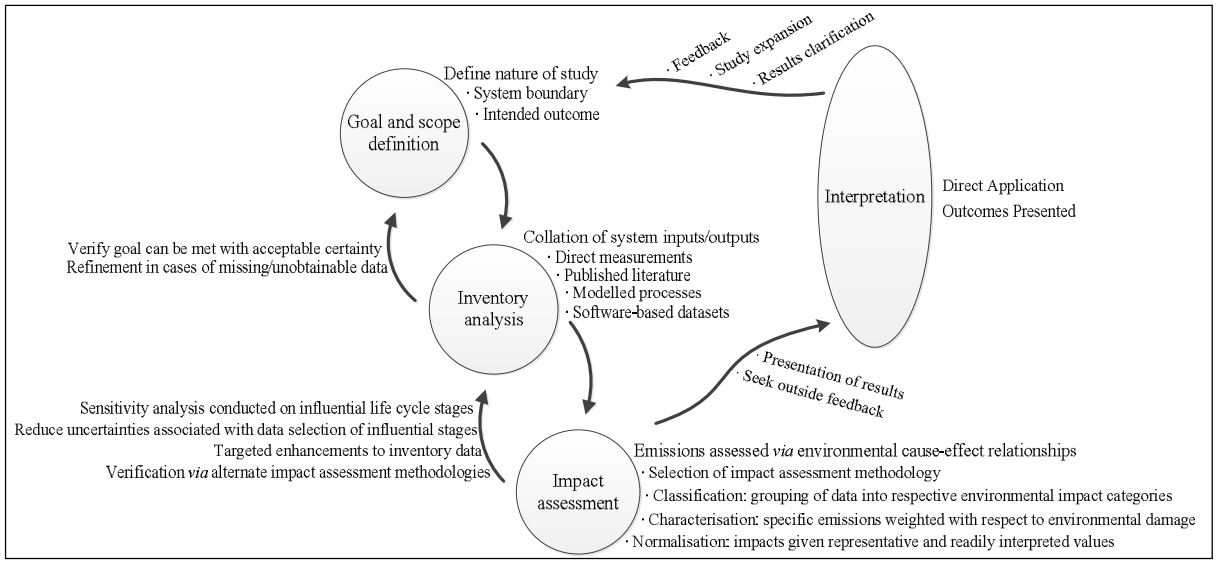


Figure 2-1 The LCA methodology, (Hetherington et al. 2013)

As detailed in the ISO standards, the four key steps of the LCA process are:

1. Goal and Scope

The initial demand for an LCA study to occur will be driven by the need to quantify the impact of a particular product or system. Exploring this question brings to the fore technical boundaries for the satisfactory coverage of the system, and defining the particular function in which is being performed.

2. Inventory

In short, data collection. Inventory step involves the acquisition of representative the flows within the defined system boundary. A life cycle inventory can often be an early output of the LCA process. Limitations of this step are often related to difficulties in data acquisition, cut-offs, and time-restraints placed on those conducting the studies (Hischier *et al.* 2005a).

3. Impact Assessment

The life cycle activities identified in the inventory stage will very likely have associated resource use and waste flows. The impact assessment step considers all of these discrete activities in two stages:

Classification groups life cycle emissions and resource usages into comparable impact categories, e.g. proven greenhouse gas pollutants, those with ozone depleting properties etc. Or occasions within the life cycle where the consumption or usage of specific resources (natural or otherwise) has occurred, e.g. water, land usage, fossil fuel reserves etc.

Characterisation then summates the individual impact-specific pollutants into one impact value for the process. This occurs through either the summation of linear impacts, e.g. litres of water, hectares of land use, or through proven environmental cause-effect mechanisms. Typically when multiple pollutants contribute to an impact these are all measured against a reference pollutant/indicator e.g. for GHG emissions CO_2 is the reference pollutant, and the other GHG gases such as methane, nitrous oxide

are referenced against irradiative potential of CO_2 in the atmosphere; for IPCC these stand at 25 and 200 respectively for a 100 year duration in the atmosphere (IPCC 2007b).

Limitations of the characterisation step include the uncertainty regarding the effect specific wastes and emissions have on different environmental partitions. Furthermore, characterisation of impacts can be considered dependent on scientific and political influence. Both parties need consensus to determine what impacts are 'important' and merit consideration when assessing the environmental burdens of a product or system. Thus, there is a reliance on methodologies to be comprehensive in their coverage, and keep pace as knowledge is gained and more is learnt of different environmental mechanisms. This issue is highlighted for methane, one of the more established GHG pollutants, but recently one which has seen its global warming potential being just recently revised from 25 (IPCC AR4) to 34 (IPCC AR 5) times as impactful as CO_2.

4. Interpretation

Presentation of LCA study findings is vital and is often the only contact that the vast majority of people, including stakeholders, will have in the LCA process. This emphasises the importance of the interpretation stage, and the need to report clear and transparent results.

Each step in the LCA process can be considered to cascade into the next, however whilst a study develops from conception to point of delivery a high degree of feedback occurs between these steps, as shown in Figure 2-1. Such interplay between steps could likely include: a revision of scope in light of data scarcity, particular key impacts requiring further inventory analysis. Frequently 'final' study findings could prompt stakeholders to revisit certain aspects for additional or even more expanded assessment. It is for this reason that LCA must be completed in its entirety, with the LCA practitioner engaged with the stakeholders and not performed in isolation to those in need of the LCA results.

2.2 LIFE CYCLE ASSESSMENT OF NANOTECHNOLOGY

2.2.1 *DRIVERS OF NANOTECHNOLOGY APPLICATION*

The control, manipulation, and engineering of materials at the nanoscale have only become achievable with advances in technology spanning the past 30 years. However the insight of individuals such as Feynman pre-date this period, recognising the potential for unlocking a raft of functions when controlling matter at the atomic scale (Feynman 1960). The use of nanotechnology has already been identified with the *potential* to provide a great number of environmental benefits (Bhushan 2010), including:

- More efficient usage of precious materials, with valuable atoms not hidden inside bulk deposits of material, and instead brought into direct contact and application.

- Functional property improvement and newly identified properties advancing performance and efficiencies of technologies, e.g. electronics, catalysis, protective coatings, membranes, composite structures.

- Advances in future energy systems: solar photovoltaic cells, battery technology and gas storage.

- Environmental remediation such as soil treatment, water filtration, antimicrobial treatments.

Many of these applications are already being realised, and are set to play an ever-bigger role within society. The Project on Emerging Nanotechnology (PEN) (2011) offers the most comprehensive database for applications using ENMs, launched with 200 products in 2006. Subsequently, this figure climbed to 1,600+ by 2011, with 3,400 products predicted by the end of this decade. These databases are filled voluntarily, since producers are under no obligation to report ENM content (Klöpffer 2007), and therefore the actual amount is likely to be far higher.

Although approximate, the combined global production of all ENMs is in excess of 11.5 million tonnes, with a commercial value of approximately $20 billion (Lazarevic and Finnveden 2013). However, the dispersed nature and low-volume producers emerging

across the globe, and how these choose to categorise and publicise their materials make estimating the exact market penetration of ENMs difficult to quantify (Piccinno *et al.* 2012).

2.2.2 *THE CHALLENGES IN NANOTECHNOLOGY ASSESSMENTS*

Despite the recognised functionalities and claimed benefits of ENM exploitation, there are a great deal of environmental unknowns and potential side-effects (Fadeel *et al.* 2007). Many conclude that the net benefits of adopting ENMs need to be verified through LCA application before wider technology roll out and deeper global market penetration occurs (Olsen and Jorgensen 2006; Bauer *et al.* 2008; Som *et al.* 2010). To date the following -often inherent- aspects of ENMs are demonstrative of the need to carry out full LCAs:

1. **Increased energy intensity** is witness when manufacturing and manipulating matter at increasingly smaller scales (Gutowski *et al.* 2010). ENMs have found to be more energy intensive than any other material manufactured to date (Kim and Fthenakis 2012; Upadhyayula *et al.* 2012).

2. **ENMs will be deployed in different ways and quantities** to fulfil functions performed by bulk material counterparts (The Royal Society 2004; Klöpffer 2007).

3. **Many ENMs derive their properties from precious metals**, such as gold, silver, and platinum group. The high impact in their extraction (van der Voet *et al.* 2004) and concerns that their integration into nanoproducts make their recovery and recycling more difficult (Olapiriyakul and Caudill 2009).

4. **The methods of production, integration, usage profile ENMs are constantly emerging and evolving**, likened to the growth of the semiconductor industry (Klöpffer 2007). Where, in accordance to "Moore's Law" (Moore 1965), technology advancement and process developmental cycles are in the region of 18 months (Kunnari *et al.* 2009).

5. **ENM release during the life cycle.** Some ENMs are used in dispersive means (Bauer *et al.* 2008) their release is thus better understood. However, for fixed and composite ENM integration the likely release points are not so obvious. Some

consider the manufacturing stage is likely to carry the greatest likelihood of exposure Som *et al.* (2010), and again during end-of-life disposal, shredding, incineration and landfill (Bauer *et al.* 2008). However, Gottschalk and Nowack (2011) conclude that releases are likely to occur across the whole life cycle of a product from both dispersive applications, and fixed particles released through wear and degradation. This represents not only lost resources difficult or impossible to retrieve, but also the introduction of new waste streams in the biosphere (Bauer *et al.* 2008).

LCA provides a framework where the above could be fully appreciated and quantified. However, there remains additional unknowns preventing the fuller impacts that ENM usage may entail, of note:

6. **Uncertainty regarding the environmental and human health impacts of ENMs** (Oberdörster *et al.* 2005; Som *et al.* 2010). The unique properties come hand-in-hand with unique risks (Fadeel *et al.* 2007). Increased uptake in toxic materials has been seen since they demonstrate favourable functionalities, for example, cadmium and arsenic compounds present in quantum dots (nano-crystalline materials), with potential uses range from solar cells, LEDs and human ingestion for medical imaging techniques (Stern and McNeil 2008). Further complexities, arise from materials typically benign at bulk scale exhibiting toxic behaviour when used at nanoscales, e.g. gold revered for millennia due to its untarnishable nature, is in fact highly reactive in a nanoparticle form (Asharani *et al.* 2010). Furthermore, use of materials such as carbon nanotubes could potentially lead to health effects akin to asbestos (Oberdorster *et al.* 2007; Hirano *et al.* 2008) .

7. **Exposure, transport and fate of ENMs are not wholly quantified** in any environmental media; soil, air, water (The Royal Society 2004; Gottschalk and Nowack 2011). Furthermore, concerns over fate are exacerbated when studies, although incomprehensive, show evidence of ENM uptake in living animal and plant cells (Oberdörster *et al.* 2005; Scown *et al.* 2010). Many note that the diminutive size of ENMs allow freer passage into living cells and organisms (Buzea *et al.* 2007; Tian *et al.* 2008); compounded when the materials used are already toxic in nature (see previous point). Metrology and monitoring

equipment are thus far not equipped to measure and track these particle releases and eventual fate (Gottschalk and Nowack 2011).

8. **End-of-life activities for ENMs are in their infancy.** There is uncertainty and debate over how nanotechnology disposal should be regulated, and how effective existing waste water treatment and municipal waste incineration are at dealing with ENMs (Breggin and Pendergrass 2007; Franco *et al.* 2007; Bauer *et al.* 2008). WWT has shown the inability to deal with certain ENMs (Brar *et al.* 2010) whereas MWI practices have proven to be effective removing and filtering in excess of 99% of the waste streams including ENMs (Burtscher *et al.* 2001) . General consensus seems to suggest E-O-L activities are effective at removing the majority of the risk, however the fraction that remain might well be unacceptable once we learn more about the potential hazards of ENM release (Bauer *et al.* 2008). Concerns have been raised over existing waste treatment streams being unable to differentiate and separate the materials, with the recovery of valuable components more difficult and less likely (Breggin and Pendergrass 2007).

   In 2012 the first ENM-specific British standard was created, however, the instructions are more ebbing on a precautionary approach with treatments akin to other chemical substances rather than the development of new practices (BSI 2012).

2.2.3 *RECOMMENDATIONS SPECIFIC CHALLENGES IN THE FIELD*

The LCA methods available to practitioners are equipped in dealing with ENM-specific impacts. However, the conduct of a complete and representative LCA are mostly incomplete due to lacking coverage of inventory data and source pathway impact assessment knowledge. Appreciably, these are awaiting consensus and creation of documented and characterised effects on existing –and potentially new – environmental impact mechanisms. Hischier (2013b) proposes a framework from ENM inclusion into current LCIA databases, however, these are some way yet from delivery.

Despite evident LCA issues, and in accordance to the recommendation of LCA field experts (Klöpffer 2007), LCAs are still very much needed at this point of time. The

appreciation of 'conventional' impacts arising from material, energy and environmental releases across the life cycle of ENM applications will form a valuable initial insight. If the 'known unknowns' are found to be unfavourable compared to similar functions fulfilled by existing systems then the case for their adoption is hampered, even before considering the 'unknown unknowns' of ENM release.

There is agreement amongst leading LCA experts, that the current framework of LCA, as laid out in the governing standards (ISO 2006a), is applicable for ENM assessments (Klöpffer 2007); however, the authors stress that operational issues are present. These issues are clearly stifling the field as reflected in the scarcity of LCA studies, despite the motivation for appreciating whole life cycle impacts, and already recognised benefit in appreciating the environmental implications of nanotechnology rollout.

Recent reviews addressing the current literature status all identify common pitfalls and extra challenges in the application of life cycle frameworks and assessments of the emerging ENM classes (Bauer *et al.* 2008; Meyer *et al.* 2009; Som *et al.* 2010; Gavankar *et al.* 2012; Hischier and Walser 2012a; Kim and Fthenakis 2012; Upadhyayula *et al.* 2012; Meyer and Upadhyayula 2013).

2.2.3.1 Goal and Scope:

Klopffer and Bauer conclude (Klöpffer 2007; Bauer *et al.* 2008) that the differences between ENMs and traditional materials fulfilling a functionally equivalent system need to be established from the onset of a study.

Importantly, the function being performed by the specific material requires defining for a given application, especially important when materials can fulfil multiple roles due to their multiple attributes. As exemplified by the work of Khanna (section 1.3.5), mass quantities are not appropriate metrics (Hischier and Walser 2012a) when dealing with ENMs. For example, it is possible to differ the results of a bulk material such as steel, and adapt the core dataset for an alternate application, e.g. its use as a construction material, or as a connection in an electrical device. However, due to the nature of the synthesis and preparation of ENMs, they often carry distinct qualities, most of which are determined at the point of synthesis of the material and its integration into specific products.

The only time mass quantities would be a suitable metric are in cases when comparing an accurately defined ENM type, deemed identical when formed via alternative routes (Hischier and Walser 2012a).

Recognising ENMs in their final in-situ operation is necessary, therefore the first role of the practitioner is to scope functionally equivalent applications, in order to wholly appreciate the implications. The system boundary must also be devised sufficiently to encounter all stages of the ENM life cycle. In-use impacts require balancing against not only their synthesis, but also their end-of-life activities.

2.2.3.2 Life Cycle Inventory Data:

Data availability is an issue that affects the majority of LCA studies, this is particularly prevalent for emerging technologies such as ENMs. The newness and complexity of the ENM field result in no specific inventory data is presently available in LCI databases. The task of covering the vast differences in material types, compositions, and synthesis techniques and seemingly multiple tailorable configurations. Such tasks remain unfinished for even the coverage of chemicals and other materials with long-established market presence (Hischier *et al.* 2005a; Wernet *et al.* 2009). Thus LCA practitioners to date, and for the foreseeable future, must generate representative data on a case by case basis.

As concluded by Hischier and Walser (2012a) the majority of ENM studies to date, obtained inventory data by extrapolating from non-direct sources, e.g. information for bulk material usage (Steinfeldt *et al.* 2004), the approach taken by Lloyd and Lave (2003); (2005) is the use of economic input/output data for the material constituent impacts of ENMs used, the remainder of studies have relied upon judgements, estimations and assumptions based or broader public and academic literature to make representative models.

For existing and conventional industries the pathways and techniques are, arguably, well established, enough at least for meaningful representation and coverage of key system flows and impacts. However, for ENMs the rate of change of technologies is an identified hurdle, meaning an assessment of a system might soon, as reported by Kunnari *et al.* (2009), be unrepresentative after as little as 18 months. Since the synthesis

of many ENMs are often similar to fine chemical and componentry electronics productions (Edelstein and Cammarata 1998; Gao 2004), it is likely that authors have used these as foundations for ENM dataset generation; indeed this is the case for Krishnan *et al.* (2008) modelling the formation of nano-seminconductors from existing literature in the field. Hischier *et al.* (2005a) propose that when data for a chemical process is not available they should be derived for the product system, using stoichiometric relationships and the quantification of relevant material, and energy flows related to the product being formed.

A restriction of representative rather than actual process data is the likely reason why the coverage of ENM systems in studies to date have been met with varying degrees of accuracy and detail. Although difficult to comment specifically on these by reading the studies, outputs are only presented for energy consumption, and bulk material consumption in the

Weaknesses of non-direct process data input can be appreciated in the case for the widest covered carbon-based material. The representative of the data has been questioned by many reviewing these studies to date (Hischier and Walser 2012a; Upadhyayula *et al.* 2012). When comparing the widest studied material class, energy requirements in the production of CNTs there is already an appreciably large difference, Encompassing a range varying between 2.75 TJ ($x10^9$) per kilogram in (Bauer *et al.* 2008; Hischier and Walser 2012a), and 66 MJ /kg (Agboola *et al.* 2007; Singh *et al.* 2008).

CNTs are an umbrella term covering a range of different formed properties, which appreciably different implications on the likely application. However, as Hischier and Walser (2012a) note, even between similar reported pathways the variances are over a factor of 10,000 for the high pressure carbon monoxide route, and almost 100,000 for the chemical vapour deposition route (CNT synthesis pathway assessed in chapter 4 of this thesis).

Such large degrees of disparity make subsequent analysis and predictions far less robust and meaningful. Kim and Fthenakis (2012) concur that the immature status is likely responsible for such variances in early studies, and argue that upon wider adoption of the material energy input might not be such a dominant factor. However, they stress the

need for reproducible data sources, and to verify current findings with more process-based LCA findings. Moreover, Meyer *et al.* (2009) cite an additional driver for appreciating inherent burdens prevalent in a product formation, necessary to understand before wider scale adoption of such materials. In light of this Bauer et al. (2008) call for more transparent, precise and representative inventory datasets to be produced. And these to be targeted on delivering the most relevant data, for the most widely used materials formed via the most likely production methods.

Despite the recognised benefits of process-based LCAs, only two examples from Roes *et al.* (2007) and Walser *et al.* (2011) were witnessed of direct process synthesis data being used to populate the inventory data. Further to this, however, this thesis author has added to this by the production of direct process assessments of multi-walled carbon nanotubes and metal nanoparticle catalysts in Griffiths *et al.* (2013a); (2013b).

Direct process data is preferable, since it not only affords greater accuracy in its reporting, but also allows for disaggregation between contributing process flows; of benefit when conducting follow-on assessments, and interpretation by others wishing to use the data. Additionally for the case of ENMs, the multitude of process routes will all differ, and thus gaining insight into a process specific activities and impacts in the ear Initial studies provide early insight into the potential impacts that require addressing before wider technology development Meyer (2009).

In addition to better coverage of the material and energy flows of ENM synthesis, wider coverage of operational equipment has been identified as an activity that requires inclusion in LCA studies of the field (Klöpffer 2007). The increased intensity of nanoproduct processes would imply specialist infrastructure in the, manipulation and integration, however, at present this remains unanswered, only assessed in one study. Krishnan *et al.* (2008) find impacts of infrastructure contribute 18% to the overall impact of forming the nano semiconductors, appreciably a non-trivial amount.

2.2.3.3 Life Cycle Impact Assessment:

Nanotechnology is an emerging area, and like any new field, a lag will be appreciably prevalent between new technologies and their assessment. However, an additional and seemingly unique trait of ENMs is the requirement for LCIA methodologies to be

adapted. LCIA require the ability to quantify the environmental impacts of ENMs presence in the environment and their potential effects on living organisms. Efforts are already underway in beginning to relate the results of exposure, fate and toxicity of certain ENMs to different environmental receptors, e.g. Eckelman *et al.* (2012) provides a coverage of CNT release in aquatic environments. Furthermore no impacts are related to human health or potential airborne particles; the coverage is therefore far from comprehensive in the account of ENM impacts.

Many of the current ENM LCA studies have only reported impacts in the form of energy demand and/or global warming potential impacts. As a matter of wider LCA debate the representativeness of these limited indicators, although indicative of the energy impacts of systems (Huijbregts *et al.* 2010), are inadequate in describing the total environmental implications of a technology rollout (Laurent *et al.* 2012). Meyer *et al.* (2009) emphathise the need for wider environmental coverage of the systems to date, which in light of the fact that many impact assessment methodologies exist for wider coverage of impacts (Dreyer *et al.* 2003; Pennington *et al.* 2004; Soares *et al.* 2006; Goedkoop M.J. *et al.* 2008). Due to the non-transparent and aggregated form of the majority of studies to date, subsequent LCIA methodology application will be nearly impossible or at best less meaningful.

It has long been recognised that ENMs carry with them new and unexpected properties, with likely implications on the environmental impacts of the formed materials (The Royal Society 2004). There are no current LCIA specifically for ENMs. Only three studies identified considered the life cycle implication of ENM-specific flows. Hischier 2013 CNT, Walser 2011 nano silver, Kohler 2009 CNT across life cycle.

2.2.3.4 Recommended approach for Nanotechnology assessment

Despite the lare uncertainties that are prevalent due to the small amount of complete LCAs to date, there is broad and unanimous consensus in the activities that an LCA practitioner would need to undertake when assessing ENM materials.

1. Direct process measurements of an ENM production route

2. ENM material/product to be compared on a functional basis to exisiting or alternative systems for meaningful insight into the assessment.

3. Detailing of sources, and nature of ENM releases, both potential and likely across the life cycle

4. Adequate coverage of system to include an end-of-life activity.

2.2.4 *NANOTECHNOLOGY LCA STUDIES TO DATE*

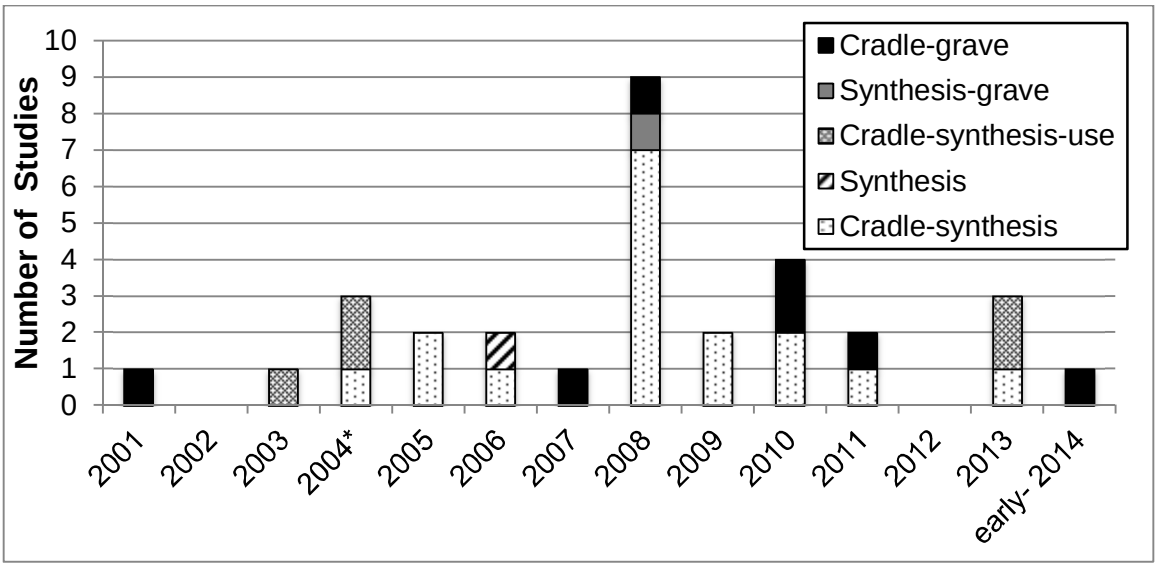


Figure 2-2 LCA studies to date on ENMs

A key cornerstone when attempting to address the objectives of this thesis, was to appreciate the nature of the LCA studies in similar fields to date. A literature survey was conducted: firstly to establish whether similar studies existed of the engineered nanomaterials (ENM) being investigated, furthermore, to appreciate how others have preceded and addressed the unique challenges that face ENM technology assessment. The first identified LCA of an engineered nanomaterial (ENM) occurred at the turn of this century (Greijer *et al.* 2001) it is therefore a relatively new field of research. Indeed, since this time (early 2014) the author has only identified 31 case studies within 25 publications, (consisting of journal peer-review, commissioned reports, book chapters and conference proceedings), shown in Figure 2-2. The majority of these studies up to 2012 have been detailed within the reviews of (Gavankar *et al.* 2012; Hischier and Walser 2012a; Lazarevic and Finnveden 2013), since this time the author has added three more, two of which are the author's own work Griffiths *et al.* (2013a); (2013b) and a study by Wang and Yuan (2014).

2.2.4.1 Cradle-to-synthesis assessments

As seen in Figure 2-2, the majority of studies have focused on the cradle-to-synthesis impacts of forming ENMs. Upadhyayula *et al.* (2012) comment on the positive merit of LCA application at this point, in the case of CNTs many alternative synthesis routes are available and thus early feedback and evaluation of these routes is highly beneficial. The widest rolled out technologies to date are carbon based, and nanoparticle metal oxides Meyer 2009 (Meyer *et al.* 2009). The coverage of ENMs in LCA studies reflect this, as shown in Figure 2-3.

Therefore, the work of Healy *et al.* (2008) who consider the three most developed routes in the manufacture of 1 g of carbon nanotubes (CNT), and Kushnir and Sandén (2008) consider the gate impacts of wider carbon-based CNTs are informative to many interested in the use of these materials. Furthermore, Singh *et al.* (2008) considers two conceptual processes for CNT growth.

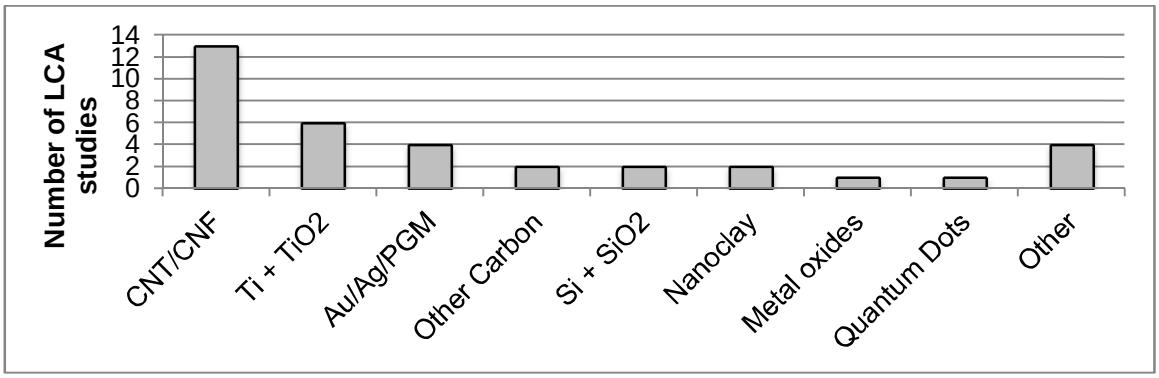


Figure 2-3 ENM material types assessed using LCA (from studies covered in Figure 2-2)

Despite LCA being applied more to CNTs than any other class of materials, the coverage was insufficient for use in this thesis, which is discussed specifically in chapter 4 where the synthesis of multi-walled carbon nanotubes are assessed.

The coverage of cradle-to-gate impacts have merits, although they do not answer the wider questions regarding the replacement of existing industries and systems with functionally equivalent ENM solutions.

2.2.4.2 Cradle-through-use assessments

The importance of whole life cycle consideration and comparison of systems is a strength that LCA affords. However, to date only six of such examples have occurred (Hischier and Walser 2012b), and is especially necessary, when considering the already high energy intensities, and cradle to gate impacts being reported (Gavankar *et al.* 2012). ENMs are not likely to be deployed to replace conventional materials on an equal mass basis, instead their adoption is likely to be in smaller quantities, and as part of composites, coatings, or active ingredient owing to their unique properties (Bauer *et al.* 2008). This means that it's of utmost importance to determine the intended function an ENM is to fulfil in order to gain a holistic understanding of the material's overall life cycle implications (Klöpffer 2007).

The work of Khanna *et al.* (2008); (2009) is an illustrative example of why system-wide coverage and adoption of a suitable functionally equivalent system is essential when assessing nanotechnologies. In the first related study of Khanna *et al.* (2008) the synthesis route and mass production of carbon nano fibres (CNF) is assessed; materials which rank amongst the highest in terms of stiffness and strength properties. Khanna conclude the production of CNF is many orders of magnitude more energy intensive than traditional materials such as steel and aluminium.

However, in their follow-up study Khanna and Bakshi (2009) hypothesise an in-use application of CNFs, replacing steel car body panels with equally strong panels from composites containing small mass fractions of CNF. The results were panels up to 62% lighter than steel. Furthermore, by expanding the scope to an in-use phase, the lighter vehicle resulted in proportional fuel savings, which over the course of the vehicle's lifetime was great enough to offset the higher embodied energy of the CNF containing panels. A similar finding was also presented by an earlier study (Lloyd and Lave 2003), whereby the USA fleet-wide adoption of nanoclay composites in place of traditional steel and aluminium panels were considered. An end of life activity was not undertaken in either study (Lloyd and Lave 2003; Khanna and Bakshi 2009) and although the authors note that the recycling of nano-composite panels would be more difficult, with less opportunity for recycling, no quantitative assessment was conducted, and thus the whole life cycle benefits of adopting the materials could not for certain be presented.

LCA has also been used to assess alternative photovoltaic (PV) cell technologies incorporating ENMs (Sengul and Theis 2010; Kim and Fthenakis 2011); quantum dot, and nano nanocrystalline-Si CdTe, and silver respectively. In both of these studies the production gate impacts of the ENM solutions were higher than conventional PV module, however, enhanced generating efficiency of the ENM-modules see an overall benefit when their in-use adoption was considered. However, Sengul and Theis (2010) note that when considering heavy metal emissions QD manufactured cells was the most polluting technology, demonstrating that energy-savings is not the only relevant indicator when considering the adoption of ENMs.

2.2.4.3 Cradle-to-grave assessments

To date only a handful of studies were identified as conducting whole cradle-to-grave assessments. (Greijer *et al.* 2001) again consider a PV application, however it is difficult to appreciate benefits of ENM technology adoption due to no comparative assessment available in their study. However, Bauer *et al.* (2008) conducted such a study between different television technologies. Although a largely theoretical based study, it showed field emission screens incorporating CNTs would be lower impact than traditional LCD and cathode ray television sets. These findings were based across a whole life cycle, though only include 'classical' energy and material flows and no specific ENM-impacts; and have very little LCI data for the ENM elements.

Examples of considering wider ENM-specific life cycle implications, were covered by the most comprehensive examples in the studies of Köhler *et al.* (2008); Walser *et al.* (2011) and Hischier (2013a). Although not specifically measuring performance attributes, Kohler et al. assess the use of CNTs within a dispersive application of clothing/textiles and a composite application within Li-ion battery technologies; providing an in depth breakdown of where ENM release pathways were likely across the life cycle.

Walser et al. and Hischier are the only examples where ENM-specific impacts are quantified in the context of the whole system life cycle; looking at nano-silver in clothing, and CNT impacts as part of a television set (expanded from Bauer *et al.* (2008)) respectively. The impact categories were limited, although the authors deserve high credit for this rare inclusion. In these cases the nano-silver impacts were deduced from

studies conducted on risk assessment data, similarly a USETOX (rosenbaun) based model on the work of Eckelman *et al.* (2012) measured the effect of CNT release into water.

ENM-specific releases were found to be minor in the context of a whole LCA based on these few isolated initial studies. The model used by Hischier and developed by Eckelman *et al.* (2008) sought to address the question of whether CNT production or CNT release presents the most environmental impact. The study concluded, that even for worse case CNT release scenarios, the production phase is of equal if not greater burden, highlighting the need for more work to be conducted to investigate synthesis routes of CNTs.

For the ENM studies mentioned here, it must be stressed that this was for limited scope of assessment, only considering the release into aquatic environments, and are founded on the present state of ENM toxicitiy knowledge; where it can be appreciated to be lacking in widespread scientific consensus (Ray *et al.* 2009; Boverhof and David 2010). However, these are important findings, and the continuation of such work will be of importance in providing a wider insight into the holistic effects of ENM exploitation.

It would be advised to wait until wider acceptance of characterised impacts of ENMs is achieved and subsequently provided in LCIA methodologies. Otherwise, disparate findings and presentations of wide-ranging impacts between studies could occur.

2.3 EMERGING SYSTEMS

In achieving much of the purposes of this thesis there is a need to derive functionally equivalent models in order for comparative assessments to occur with exisiting technology systems, and indeed between the different case studies under investigation. The processes investigated, however, are at the early stages of development, and have appreciably not left the confines of laboratory practices and scales. Upscaling and forecasting of these impacts are indeed necessary in order to provide meaningful assessments of the technology performance.

Very few examples of LCA being applied to scaling up of technologies. With no identified framework, with choices seemingly down to the judgment of the investigator into the specific process at hand.

Examples exist in estimating the impacts of established systems at different scales (Caduff *et al.* 2012), however, in such cases differents major activities involved will not significantly vary across wider scales of development. Therfore, the creation of robust datasets and well considered scenarios for wider scales will be sufficient. For an emergent system where no previous or comparable systems seem appropriate or obtainable, this approach becomes very difficult and subject to high levels of uncertainty.

Shibasaki *et al.* (2006); (2007) detail considerations of assessing the scale-up of laboratory and pilot scale processes. The major considerations outline in Shibasaki's work is the consideration of the processes as a system rather than linear pathway through synthesis and manufacturing steps. Additional considerations include the differentiation between direct and auxillary activities and equipment, recycling of materials. The processes are insightful, however, are arguably methods that would be conducted by many researchers during the sensitivity and interpretation steps of the LCA framework.

This thesis author co-wrote an article summarising many of the issues prevalent for nano and wider emerging fields (Hetherington *et al.* 2013).

2.4 THE LIKELY SOURCES OF CO_2 FOR USE

CO_2 is being released at many disparate point sources across the globe, and is indeed accessible everywhere with its presence in the atmosphere, it is for this reason that air-capture technologies have gained interest (Stolaroff 2006) and are at least a theoretically viable CO_2 sources for the future (Lackner 2009). However, air capture is theoretically 3.4 times more energy intense than sources, such as fossil fuel flue gases, with 10% concentration of CO_2 (Keith *et al.* 2006), and is lagging behind progress of direct point-source emitters of CO_2. In this thesis, CO_2 is modelled specifically as coming from the post-combustion carbon capture (CC) from fossil fuel electricity generation plants, arguably, the most likely initial CC technology to make significant headway (Metz *et al.* 2005).

The avoidance of direct CO_2 release into the atmosphere, thus reducing the GHG impact of fossil fuel combustion, is the primary objective of CC technologies.

Typically, the reporting of life cycle impacts of CC technologies are concerned with the unit increase in impacts (typically GHG or energy demand increase) with relation to the power being generated at a power plant, e.g. impact change per kWh electricity produced at the plant (Odeh and Cockerill 2008). However, from the perspective of CO_2 use as a feedstock, the flows require consideration for the functional unit of the CO_2 captured. A full LCA pertaining to a 'unit captured CO_2' FU could not be found, therefore a dataset has been formulated based on the work of others in the field investigating CC technologies.

2.4.1 *LCA FOR CCU*

LCA is a very suitable tool for calculating the overall performance of carbon capture technologies, since it not only accounts for the direct GHG benefits of preventing the release of CO_2 into the atmosphere, but also weighs these benefits against the GHG and other environmental impacts incurred in achieving this. The capture of these impacts is essential when considering the downstream use of CO_2 as a feedstock. The use of LCA as a key assessment tool for potential carbon capture and utilisation (CCU) technologies is unquestionable, and identified by many to be the only quantifiable way of establishing whether or not processes are successful in their CCU goals (Aresta and Dibenedetto 2007; Centi and Perathoner 2009; Centi *et al.* 2011; von der Assen *et al.* 2013). LCA, unlike other environmental management tools, allows the shifting of environmental burdens of a system to be quantified (McManus 2001). The capture of CO_2 from a point source represents a beneficial environmental activity at that time and place, however, there is a need to track the additional environmental impacts are incurred from preventing this CO_2 from re-release into the atmosphere, and to evaluate that all life cycle activities are less impactful than the unhindered release of CO_2 in the first instance. LCA can answer this, not only from the perspective of CO_2 emission impacts, but also wider environmental impacts arising from the technical systems and their burdens on the environment.

To date very few examples of life cycle thinking being applied to CCU have been found (von der Assen *et al.* 2013). Therefore at present, a gap in knowledge exists in appreciating the potential environmental benefits such systems could afford. The emerging nature of this field and lack of operating information for CCU processes, at lease at any meaningful scales, are arguably the reasons for this knowledge deficit. LCA is data hungry, it is for this reason that LCAs are typically performed retrospectively; when systems are operational and information is more readily available (Hetherington *et al.* 2013). However, as discussed, LCAs are arguably at their most effective when they are employed as part of an emerging technology steering tool, as shown later in section 3.5.

Early stages of development are the most flexible in adopting change and optimization (Bhamra *et al.* 1999). Those working in the fields of CO_2 chemistry need the confidence, or at least appreciate the value, of making process information available for LCA. The use of raw inventory data will afford greater insight into the 'CO_2 abatement avenue' that CCU is attempting to navigate.

Technology solutions are coming from various fields and at various scales of development, with limited commonality between them, as seen in the case studies investigated in this thesis. Appreciably these solutions will also be at varying scales of development. However, LCA allows competing studies to be assessed on a functional unit basis.

Studies exploring enhanced oil recovery (EOR) via CO_2 injection in the Norwegian Sea (Hertwich *et al.* 2008) and are showing environmentally favourable potential in not only GHG abatement, but also in reduced intensity of extraction activities, mitigating more impact per kg of extracted oil. A feasibility conducted by Soltanieh *et al.* (2009) of Iranian oil fields conclude similar findings with regard to 1 kg of CO_2 injection yielding 6-8 additional barrels of crude oil. These are competing industries for the CO_2 feedstock, and such LCA work is a necessity to gain balanced accounting of the options. Indeed perhaps CCU will reside in applications where EOR is not feasible, and rather than simply disregard the CO_2 for that function its use as a carbon feedstock should be explored. To re-iterate the sentiments expressed by von der Assen *et al.* (2013)"all environmentally beneficial CO_2 utilization pathways should be employed".

2.5 SUMMARY

This chapter has provided a brief account of the life cycle assessment (LCA) framework, with justification for its application and suitability in answering the main objectives of this thesis. Through the iterative steps of: goal and scope definition, inventory data generation, impact assessment results and interpretation stages. LCA's systematic approach provides insight via quantitative means into the inner workings of a performing system, appreciating what part the material, energy, production and waste flows have on the overall impact. This insight provides an opportunity to better manage and mitigate impacts. Adequate system boundary coverage relating impacts to a functional flow or activity allows comparative assessments between similar performing systems to occur.

2.5.1 *LCA FOR NANOTECHNOLOGY*

An overview of work currently in the field of LCA's application to nanotechnology and engineered nanomaterials (ENM) was presented. Relatively few examples of studies applied to nanomaterials were found, and of these considerable gaps were prevalent in their holistic assessments. Amongst the chief identified reasons for gaps and uncertainty in the knowledge are:

- **Materials being assessed in isolation**, without considering a potential in-use application. The need for comparative assessments to occur between ENM applications and conventional technical functions fulfilled by existing systems is necessary.

- **Data gaps for ENM-specific life cycle activities** exist along the whole life cycle: the material flows that occur through production and manufacturing techniques, in-use application, and end-of-life activities. These appreciably differ on a case by case basis, and getting data has proved difficult, resulting in studies conducted having different levels of coverage and representation.

- **Environmental impact uncertainties and unknowns regarding ENMs.** The release of ENMs are likely to occur, dependent on application, across the whole

life cycle of a product. At present time the impacts that the multiple types of ENMs may have on the environment are unknown.

- Amongst the major recommendations for addressing the knowledge are more case studies of ENMs, transparent in their nature and formed using direct process data. Assessments of ENMs fulfilling functional roles are also missing. The work within this thesis addresses these issues.

2.5.2 *LCA FOR EMERGING SYSTEMS*

The comparison of emerging systems with established industrial processes is a hurdle when conducting comparative assessments. No firm guidance or framework was found, and examples of LCA being used to predict the impacts of systems at different scales were scarce.

2.5.3 *LCA FOR CO_2 UTILISATION TECHNOLOGIES*

LCA has been recognised as a key tool for assessing the impacts of capture and utilisation (CCU) technologies. The major drivers and benefits for CCU were outlined, identifying current motivation for its potential adoption in meeting societal demands. LCA provides a means to wholly quantify the shifting impacts of CO_2 abatement from the atmosphere and subsequent transformation. The need for early assessments will allow comparison against other CO_2 abatement technologies, and challenges in competing markets for the use of CO_2.

The findings of this work has shaped the approach taken for addressing the different objectives of this thesis; from robust inventory and impact assessment of formed ENMs, their application in CO_2 utilisation technologies comparisons between competing CO_2 using processes, and wider industrial systems.

Chapter 3: RESEARCH APPROACH

"Where you've been is not half as important as where you're going." - Anon

This chapter outlines the toolkit/approach used to measure the life cycle performance of different materials and processes assessed in this thesis:

- the specific life cycle inventory datasets and impact assessment methodologies used
- producing inventory data when missing or inaccurate for the formed materials, electricity use, infrastructure equipment
- approach for assessing the impacts of products formed via CO_2 conversion technologies, and the overall GHG mitigation of carbon capture and utilisation technologies.

3.1 APPROACH INTRODUCTION

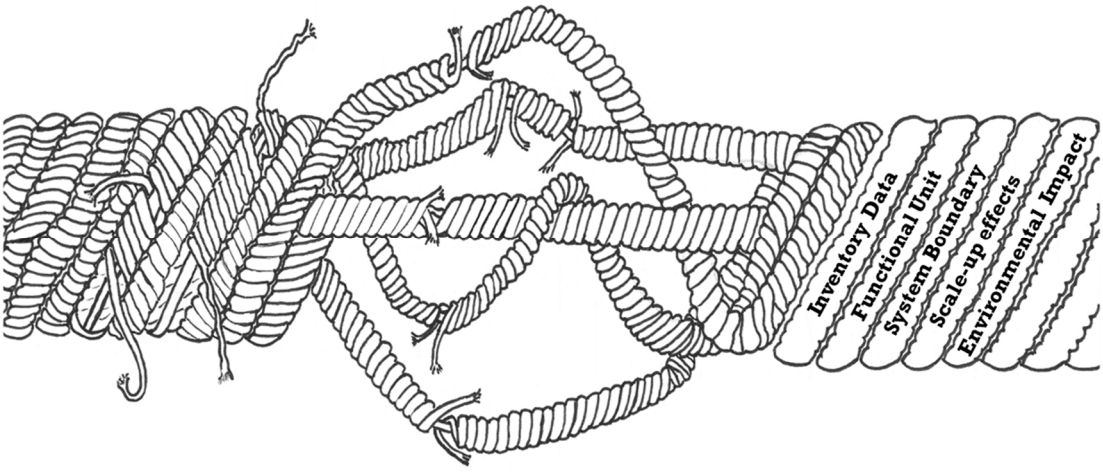


Figure 3-1 LCA as a rope (Hetherington *et al.* 2013)

If one were to consider the analogy that LCA is a rope, pulling technology developers, and decision makers on a pursuit towards sustainable pathways; The rope (LCA) itself is made by the pulling together of a great many elements in the provision of a robust account of the environmental implications of a particular product or system. The integrity of the rope is dependent on the entwined elements; uncertainties can be considered the fraying of such elements.

As with any rope, the extent of fraying can lead to breaks, in the best case this result is an LCA study halting in its tracks, or the results being meaningless. Moreover, the worst conceivable outcome is a rope charged with enough energy to cause damage. The backlash of a broken LCA could be considered misinformation and ill-represented potential impacts of system, dangerous for the system at hand and the wider integrity of the LCA methodology.

Trust and integrity are utmost values to be upheld when conducting and LCA required, uncertainties or arguably the lack of highlighting uncertainties have led to many decision makers not trusting LCA to be a reliable tool (Herrmann *et al.* 2014).

This chapter lays the foundations of the approaches followed the assessments conducted throughout this thesis.

3.2 STANDARD INVENTORY DATASETS USED IN THIS THESIS

When the majority of practitioners conduct LCAs they use reference datasets to represent materials being used in the system, more often than not this occurs for activities upstream and downstream of the technical system being assessed. Obtaining the information for the exact flows associated with a system would be arduous if, arguably, impossible to achieve. Conducting LCAs from first principles would also severely hamper the use of the tool, slowing the rate in which studies could be conducted, increasing the efforts required and delaying key findings reaching those in want of the information.

When assessing background systems and materials entering the system boundaries of the LCA studies, this thesis uses life cycle inventory datasets of Ecoinvent Database v2.2 (2010). Ecoinvent is a valuable dataset, covering the major and significant technical systems they allow the coverage of a product life cycle to occur with satisfactory levels of accuracy. Moreover, the use of Ecoinvent presents disaggregated process information, providing the breakdown from the different contributors such as energy use, materials, auxiliary processes, emissions etc. Such insight provides an appreciation into their relative contribution in the whole context of the product/system. The majority of which should be similar for all commonly formed materials once the production routes have been established (or not) as being a close fitting match to the actual product being investigated.

3.2.1 *LIMITATIONS OF 'OFF THE SHELF' INVENTORY DATASETS*

Limitations arise from using reference LCI databases. Firstly the results aren't necessarily representative of the *actual* process assessed. For instance when wishing to account for a certain material being used by a process, the database might have coverage of this material's production route at one location/factory/plant. This data is used for many studies, despite the actual material being used very likely not coming from this referenced location. With this limitation stated, the major and indicative impacts are covered through using the representative dataset, thus providing a sound quantitative estimation.

For studies conducting comparative assessments between competing products/systems, the consistent use of datasets for both limit the uncertainties of the LCA results. e.g. if both use steel, then the impacts will be consistent

The number of accessible and peer-reviewed life cycle inventory datasets is expanding[3], however, the combination and multitude of materials, products, and industrial processes in the modern world are vast, ever increasing and evolving. Thus the availability of a dataset pertaining to a specific substance or process formed from a prescribed pathway is not always available to practitioners.

The temporal, spatial, and static nature of LCA datasets, once data is captured and presented it is very likely to be specific to a certain industrial system the practices of a company/country, and appropriate for the activities assessed at that point in time. Thus, when possible, the collection and presentation of primary data from the direct origin-specific process is preferential to standard inventory datasets. When this was not possible, the sensitivities of the reference datasets, their impacts on the overall LCIA impacts are investigated to ensure the data is best representative of the specific materials and processes under investigation.

3.3 IMPACT ASSESSMENT METHODOLOGIES USED IN THIS THESIS

The key output of an LCA is that the impacts of the technology investigated can be presented in terms of characterised and interpretable environmental damage indicators. This thesis was concerned with carbon capture and utilisation technologies, arguably carbon accounting or footprinting would suffice, however this was deemed a shortcoming of the potential contribution that the LCA process affords. Therefore a multitude of environmental damage indicators were used. In this thesis two separate impact assessment methodologies were used:

- ReCiPe Goedkoop M.J. *et al.* (2008), includes the IPCC (2007a) recommended global warming potential values)
- Cumulative Energy Demand (CED)

[3] As this thesis research entered its closing stages Ecoinvent version 3.0 was rolled out. Appreciably, covering more processes in more detail.

3.3.1 *ReCiPe*

An abundance of LCIAs are in existence, in this thesis the ReCiPe methodology has been used for the provision of the majority of environmental impacts (Goedkoop M.J. *et al.* 2008). In summary, ReCiPe, at the time of conducting the LCA work contained in this thesis, was found to be the most comprehensive LCIA, concerned with wide-ranging environmental damage indicators for a broad spectrum and appreciation of other environmental factors at play. Providing transparent reporting on mechanisms and characterisation factors, ReCiPe, is a combined and adapted incarnation of the Eco-Indicator 99 (Goedkoop and Spriensma 1999; Goedkoop and Spriensma 2001) and CML methodologies (Guinée 2001) and constructed under the guidance of many leading field experts (Goedkoop M.J. *et al.* 2008).

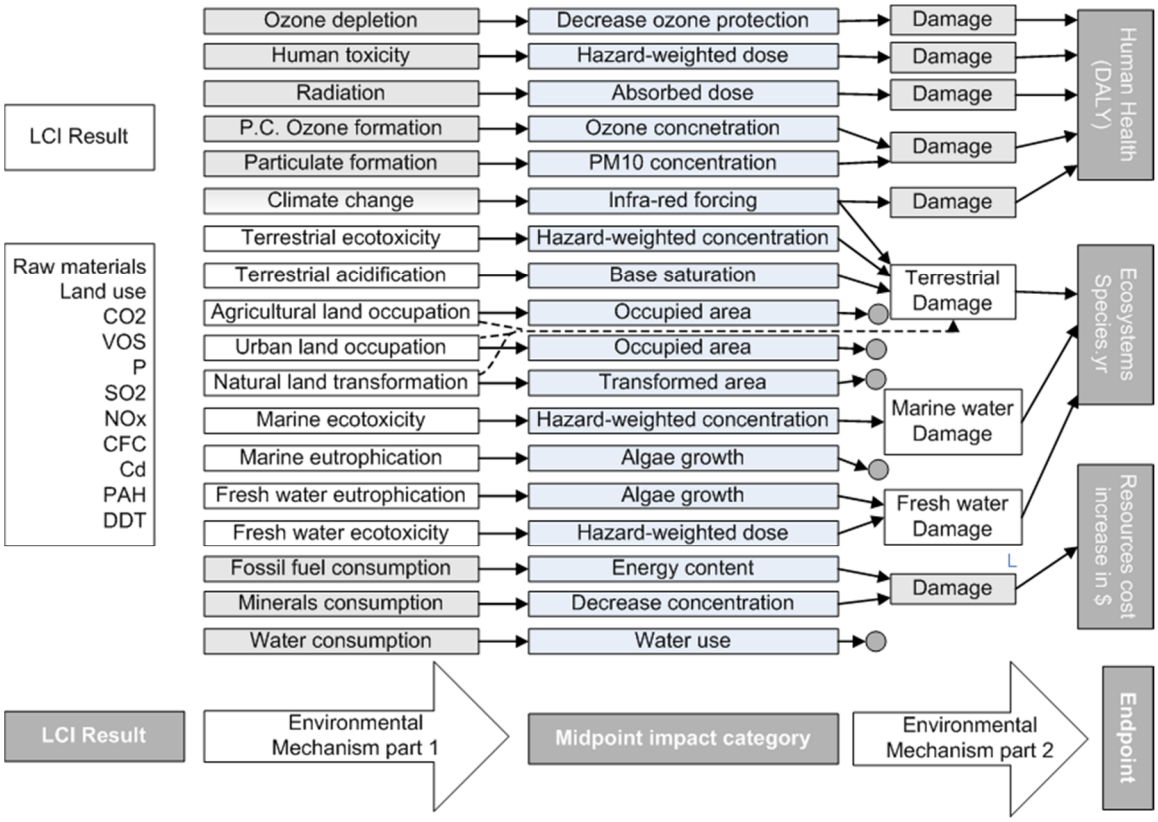


Figure 3-2 Overview of ReCiPe methodology.

As shown in Figure 3-2, within ReCiPe is the option of considering 18 midpoint and 3 endpoint categories, the latter is essentially the distillation of 18 impacts into three over-arching indicators, reporting damage to: human health, ecosystem diversity, and resource availability. This involves grouping two or more impacts into the respective

endpoint categories. The 18 midpoint indicators, shown in Table 3-1 assess the climate change impacts, as per the guidance of the IPCC (2007a) impact methodology, along with in-house developed methodologies for the assessment of 17 other impacts.

ReCiPe provides impacts explicit to the cultural values and perspectives being considered (Hofstetter 1998). This thesis takes the Hierarchical standpoint, where environmental impacts are in-line with the weight of scientific thinking. The hierarchist sits approximately in the 'middle-ground' of the ReCiPe cultural perspectives. More precautionary LCIA accounting occurs with the egalitarian perspective, this standpoint seeks to minimise environmental interference to the greatest extent, considering any potential impact in its most damaging sense. Egalitarian perceived impacts could be considered scientifically less substantiated and subject to a higher degree of uncertainty to those of the hierarchist. At the other end of the cultural scale is the individualist perspective, essentially the least concerned with environmental damage. When considering the impacts as per an individualist, only undisputable cause-effect mechanisms are considered, and little emphasis is placed on limiting resource use and the impacts activities might be having on people and planet.

3.3.2 *CUMULATIVE ENERGY DEMAND (CED)*

Assessed in parallel and complimentary to the ReCiPe impacts is the CED, or net energy analysis, methodology. The premise of CED spawned in the 1970s, appreciably the early days of life cycle thinking, where energy usage was recognised as an important indicator for the overall environmental performance of a process; and still stands broadly true today (Huijbregts *et al.* 2010). In this thesis the CED methodology developed by Frischknecht *et al.* (2003) and an available resource provided by the Ecoinvent centre. The methodology is an insightful tool, providing, from the ground-up, a detailed account of the quantity of energy being consumed, from where the energy originates; be it non-renewable: fossil, nuclear, biomass from primary reserves, and renewable: wind, solar, geothermal, hydro, biomass from forest, waste and agricultural sources.

Table 3-1 Environmental impacts assessed; ReCiPe midpoint indicators and CED.

Impact Category Name	Description	Physical phenomenon measured	Indicator / reference value for impact
Climate change (IPCC method used by ReCiPe)	**Global warming potential, infra-red radiative forcing**	**W x yr/m²**	**kg CO_2 eq**
Ozone depletion	**Stratospheric ozone concentration**	**ppt x yr**	**kg CFC-11 eq**
Human toxicity ‡	**Hazard-weighted dose**	**-**	**kg 1,4-DB eq**
Photochemical oxidant formation ‡	**Photochemical ozone concentration**	**kg**	**kg NMVOC**
Particulate matter formation ‡	**PM10 intake**	**kg**	**kg PM10 eq**
Ionising radiation	**Absorbed dose**	**man x Sv**	**kg U235 eq**
Terrestrial acidification	**Base saturation**	**yr x m²**	**kg SO_2 eq**
Freshwater eutrophication	**Phosphorous concentration**	**yr x kg/m³**	**kg P eq**
Marine eutrophication	**Nitrogen concentration**	**yr x kg/m³**	**kg N eq**
Terrestrial ecotoxicity ‡	**Hazard-weighted concentration**	**m² x yr**	**kg 1,4-DB eq**
Freshwater ecotoxicity ‡	**Hazard-weighted concentration**	**m² x yr**	**kg 1,4-DB eq**
Marine ecotoxicity ‡	**Hazard-weighted concentration**	**m² x yr**	**kg 1,4-DB eq**
Agricultural land occupation	**Occupation**	**m² x yr**	**m² x yr (agricultural land)**
Urban land occupation	**Occupation**	**m² x yr**	**m² x yr (urban land)**
Natural land transformation	**Transformation**	**m²**	**m² (natural land)**
Water depletion	**Amount of water**	**m³**	**m³**
Metal (a.k.a. mineral) depletion	**Grade decrease**	**kg^{-1}**	**kg Fe eq**
Fossil depletion	**Upper heating value**	**MJ**	**kg oil eq**
Cumulative Energy Demand (not in ReCiPe)	**Energy consumption; renewable and non-renewable**	**MJ**	**MJ**

The '‡' next to impact categories indicate impacts where ENMs might very likely cause environmental damage, dependent on material release, but cannot be quantified.

3.3.3 *LCIA LIMITATIONS*

Both ReCiPe and CED are considered 'automatic' methodologies, meaning once the life cycle inventory has been inputted, a software package classifies and characterises (see

chapter 2) the different waste flows and resource uses, before producing the results. A criticism of this is that the methods are comparable to 'black-box' operations, where the answers are generated regardless of whether or not errors and omissions are present in the LCI. Therefore a considerable portion of the interpretation step involves the sense-checking of results, and conducting sensitivity analysis for the effects that the assumptions and proxy dataset use have on the results. Other case specific limitations for ENMs are that current impact assessment methodologies are lacking to account for the impacts that their release to the environment.

3.4 GOAL AND SCOPE OF THE STUDIES

For the appreciation of life cycle impacts of forming specific ENMs in this thesis, the over-arching goals of chapters 4, 5 and the beginning of 7 are to:

- establish what are the dominant life cycle activities in the formation,
- appreciate where these impacts could be minimised or mitigated when moving towards more optimised - akin to industrial - practices.

Similarly for carbon capture and utilisation (CCU), CO_2 conversion processes, in chapter 6 and 7, the overall environmental performance and feasibility of the investigated routes are explored, determining:

- the overall potential to mitigate GHG impacts,
- appreciate the other impacts incurred from the operating CCU process,
- the comparative impact of formed products with existing production routes.

For each encompassed piece of LCA work conducted in this thesis, the scope is concerned specifically with the laboratory activities. Covering all of the materials, chemicals, equipment, energy use required for the synthesis of the specific materials. Auxillary equipment, used in the lab but not directly involved in the synthesis route e.g. equipment involved in sampling, analysis, characterisation of products are considered outside of the scope. This is necessary to not only accurately account for intrinsic life cycle embodied impacts of materials and processes, but also to appreciate what

activities would remain when moving towards scaling up the process to more industrial operations.

There is every attempt to present coverage of the results within the framework of an entire life cycle, “cradle-to-grave”. Robust attributional LCAs were conducted for the gate impacts of the formed materials, the in-use activities are duely addressed for the CCU applications, and an end-of-life recycling and material recovery phase is considered; an expansion of scope necessary for holistic appraisal of the materials and processes.

3.5 Approach for Measuring the Synthesis Life Cycle Impacts of Nanomaterials

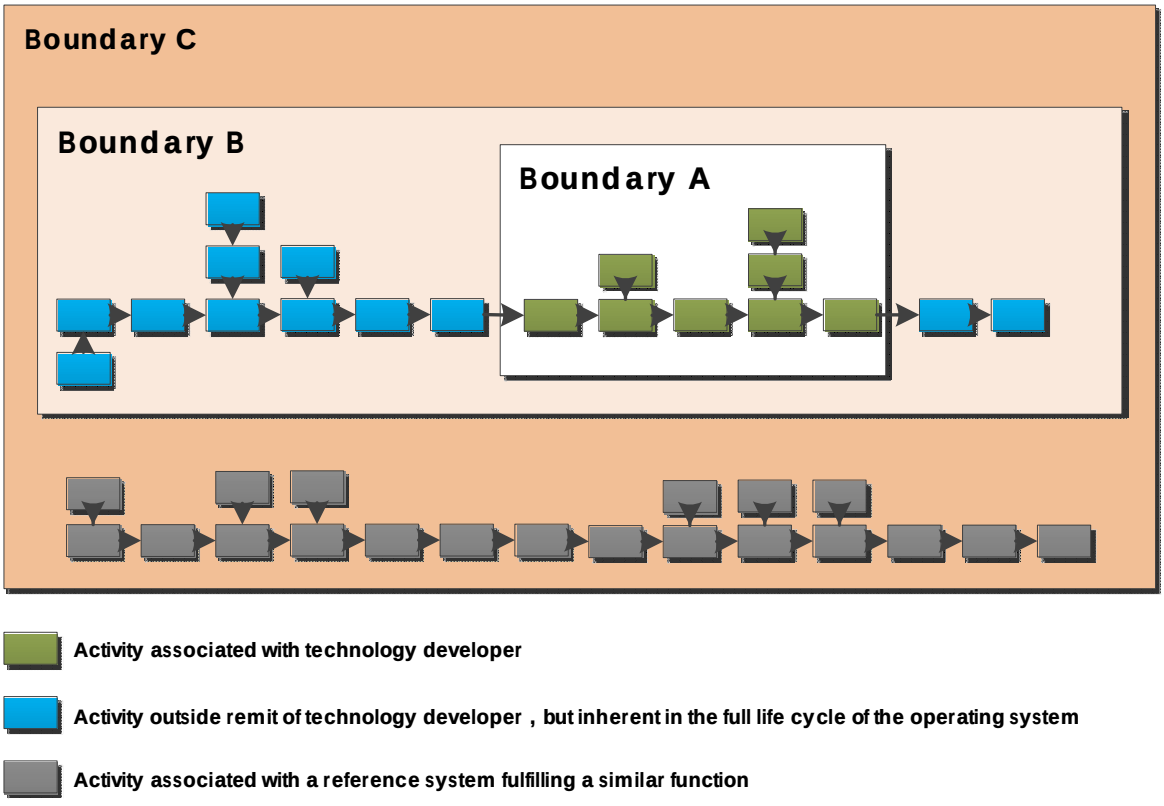


Figure 3-3 Pictorial representation of system boundaries for different LCA purposes.

3.5.1 *Goal and Scope: LCA, one tool to develop insight for multiple and wide ranging Actors.*

The initial setting of LCA study goals, and indeed the scope of assessment, for emergent technologies such as those using ENMs are different dependent on why the LCA is being conducted in the first place. Being mindful of the intended recipient, LCA

findings and results can be presented more accessible for the key actors, maximising value and impact of the work in a direct and immediate way.

Figure 3-3 shows that different, but connected system boundaries are present for the full appreciation of a system. Whilst a full LCA is required for the total appreciation of any benefits of a new technology, this information would be overly burdensome for a technology developer interested in more specific aspects of their influence on the overall process.

Thinking in this way has led to the approach to cater for the multitude of stakeholders, and those interested in understanding the impacts of nanotechnology sustainability:

Boundary A for technology developers: immediate feedback and steering towards better pathways and material selections. LCA outputs to facilitate this include identification of process hotspots and assessments of alternative materials and synthesis routes to hand.

Boundary B for wider LCA community: the furnishing of data to address identified gaps associated with the LCA of nanomaterials. The presentation of study findings and a transparent provision of assumptions and characterised impact assessment results for those assessing the use of the assessed ENM in similar, or due to their multi-application, other fields likely to use the materials.

Boundary C for further academic researchers and policy makers: Essentially providing the environmental implications and potential benefits of a proposed ENM technology in comparison to another comparable process. Helping to support a more complete evaluation (which might include social and economic aspects of a technology) of whether the technology is a likely candidate in environmental mitigation strategies.

In summary, tight ‘targeted’ boundaries are of use to the technology developer, precisely defined boundaries for other LCA practitioners, wider system boundaries and contextual implications of system for policy makers and investors. LCA is static in nature and novel technologies advance quickly, sequential ‘snap-shots’ of the environmental performance of specific processes, are vital stepping stones in the wider context of the field.

Precise and specific LCA reports should not be pigeon holed as 'niche' but considered as vital and relevant outputs. Technologies being assessed are not likely to be introduced in the immediate or medium term, thus the background data of the assessments are presented in a form that can be applied in the context of likely future energy and technology mixes.

3.5.2 *FUNCTIONAL UNITS CHOSEN FOR ENM ASSESSMENT*

In this thesis many examples exist of a quantity of synthesis ENM product being the functional unit; a batch of formed carbon nanotubes (Chapter 4), batch formed RWGS-FT catalyst (Chapter 5), or electrode coating of catalyst material (Chapter 7). These are used for the assessment of the specific production methods and materials being used, of use to the technology developer, providing an account for the relative life cycle impacts responsible in the final embodied impact of the formed product.

ENMs differ from many bulk material counterparts, the use of a mass functional unit is not best suited or indeed representative in many cases of a material's potential function.

The uses of such 'per batch' functional units require evaluation by those wishing to use the results of these studies for their own application. As recommended by others (Bauer *et al.* 2008). Results should not be taken directly, but instead appreciated in the context the system in which the ENMs are being integrated into, and the quantity required to perform a desired function. For instance, in chapter 6 MWCNT based catalysts and Fe-Pd-Silica materials are compared for a matching application, the mass quantities were not used here, but the final amount used to fulfil the operating catalysis process. Considering the many functions possessed by a material as versatile as carbon nanotubes, a full appreciation of its performance in a specific application is required, especially when compared against existing materials fulfilling the same application. Detailed characterised account of formed materials has thus been presented for the assessed ENMs, for the two-fold benefits:

- allowing others using similar material use for a similar/alternative application to verify whether material is suitably representative and appropriate for the assessed application.

- facilitating future life cycle impact and environmental risk (if any) of the material

3.5.3 *INVENTORY DATA FOR NANO PRODUCTION*

The new and emergent nature of ENMs and associated technologies is challenging the inventory production because:

- that a comparatively short passage of time has not allowed the creation of ENM datasets in reference datasets such as Ecoinvent,
- companies are not willing to share proprietary information regarding their processes, and
- the demand for the data as of yet not fully appreciated since established applications of the processes/materials have not yet come to fruition.

The following sub-sections outline the approaches taken to obtain LCI data. An overview on the decisions faced when attempting to use representative data for the LCIs is given in Figure 3-5. With all options pursued, sufficient literature surveys, knowledge of industrial synthesis routes, and/or patent data are necessary to ensure the best achievable representation is being achieved.

Due to the challenges and uncertainties in attempting to establish the likely life cycle impacts of a fledgling technology LCA is typically conducted retrospectively. As shown in Figure 3-4, most data and least uncertainty lies when there is established system data and operational processes that can be directly assessed. The LCA results of models based mostly on proxy and representative datasets, assumptions, projections and expectations will likely yield results that would differ from directly measured and established systems.

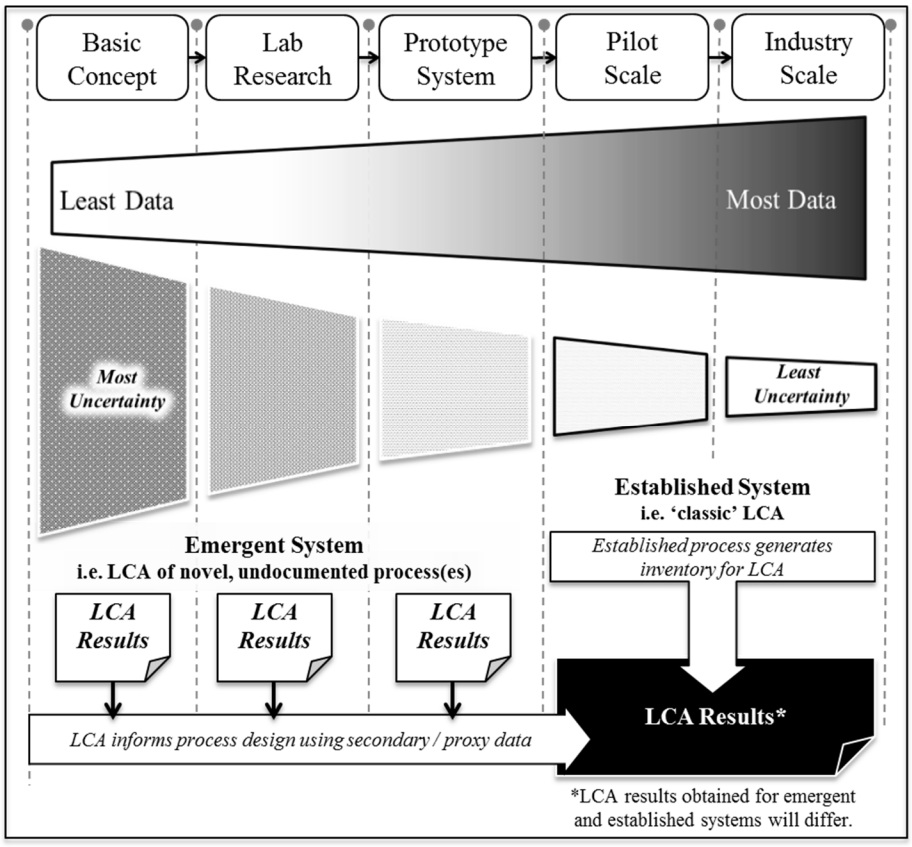


Figure 3-4 LCA applied at the early technology development *vs* established systems (Hetherington *et al.* 2013)

Despite expected inaccuracies, it is at the beginning of a new technology's research and development period where LCA is most useful in guiding system designers. LCA in its nature is very capable and powerful at the early stage of R&D in shaping decisions to avoid environmental pitfalls. Furthermore, ensuring the technology is progressed in a manner which is always aware of the potential effects that different system and operational design choices will have (Hetherington *et al.* 2013).

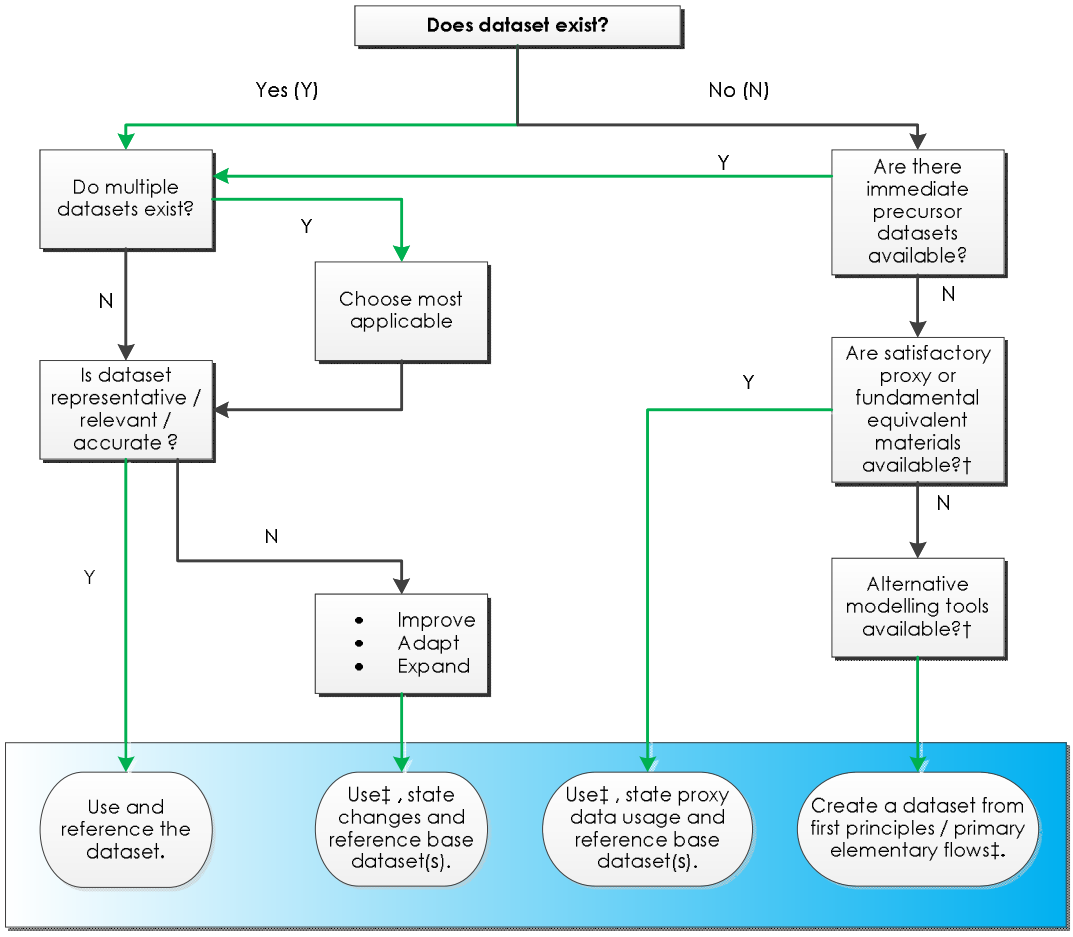
The following sections detail how this thesis has been founded on methods to reduce the uncertainty and increase the deliverable output for key decisions in the advancement of the assessed ENM-based technologies.

3.5.4 *PARALLEL LCA AND NOVEL TECHNOLOGY DEVELOPMENT*

The positive benefits of collaboration between LCA practitioner and early technology development cannot be overstated for the work contained in this thesis. The interplay between both sides meant that insight and guidance of intricate process details were relayed directly into the creation of the LCA model. Indeed, in many cases much of the inventory data such as energy measurements and flows of process materials require evaluation at the point of use and cannot retrospectively be obtained. Moreover, the LCA process and study results are better appreciated by the technology developer, widening their outlook, and changing their approach to working for the benefit of a more holistic process assessment.

3.5.4.1 Subject Matter Expert Involvement

The approach of gathering inventory data in this thesis is outlined in Figure 3-5 , and is heavily dependent on collaborative efforts in understanding and creating representative datasets suitable for describing the materials and processes being developed. When conducting LCAs on novel technologies, it was essential to gain a comprehensive understanding of the process(es) at hand, specifically the material flows, equipment used and performed function(s) of the process. However, the author of this thesis is not an expert on the novel techniques, materials and processes being developed. Indeed, it is never possible, arguably, for a practitioner to reach the same level of understanding of a process as those who have formulated the working practices and have specific field expertise in the area being investigated. The requirement for specialist expertise is especially true for the research area of emergent technologies, where the individuals developing the technology are at the forefront of understanding and sole holders of the necessary information. Therefore collaboration with the technology developers was often an essential component for the production of accurate, informative and relevant LCI data, as shown in Figure 3-5.



† Points where collaborator and subject matter expert involvement are especially required.
‡ Transparent reporting of reference consulted literature, and assumptions.

Figure 3-5 Decision tree for inventory data collection. Nano and emerging materials are very likely to be more arduous to assess, the darkening blue bar represents increasing efforts involved to obtain data.

3.5.4.2 Additional Tools to Facilitate the LCA studies

In addition to the provision of accurate laboratory data, subject matter experts were also consulted for the assessment of new datasets throughout the course of this thesis. The majority of times expert input would be from the perspective of their knowledge and judgement of how processes would very likely occur in practive. However, in the case of modelling the impacts of carbon nanotube synthesis, a gap identified in wholly quantifying the life cycle of CNTs was sufficient coverage of the feedstocks used (Upadhyayula *et al.* 2012), specifically ferrocene in the assessed route of this thesis. Literature and patent searches yielded information on a representative account of an industrial synthesis route for ferrocene, the final dataset was a collaborative effort between the author, inorganic chemist and a chemical engineering process engineer.

Full model and assumptions are presented in APPENDIX D: The ferrocene dataset used in Chapter 4 analysing the production of multi-walled carbon nanotubes, and will be useful to others in LCA fields concerned with the use of ferrocene; which has many applications such as wide fields within catalysis, and medicine,(Nesmeyanov and Kochetkova 1974; Ornelas 2011; Werner 2012).

3.5.4.3 Producing Inventory Data when they cannot be sourced elsewhere

The issue of missing LCA data is not unique to ENMs. In these instances proxy datasets were used, filling gaps in the model with data which closely represents those of the desired input, in many cases this substitution will provide a close approximation of likely environmental burdens associated with this life cycle activity.

Many examples exist in this thesis where bespoke, or adapted existing datasets are used. Instances where this has occurred are duly reported and fully described. An overview of the most common practices adopted in this research include:

- Substitution with the 'closest match', e.g. materials that are broadly similar and could be used in the intended application. E.g. graphene in place of 'glassy carbon' electrodes.
- Chemically similar, or 'near products' e.g. nafion being representative by PTFE.
- Materials formed via similar production routes, e.g. bacterial citric acid production analogous to ethanol fermentation.
- Stoichiometric analysis, to establish molar relationships between the products used and the reactants needed to create them.
- Appreciation of process enthalpies to determine that likely additional life cycle activities which may occur from heating.

3.5.4.4 Finechem

With a lack of LCI data pertaining to certain hydrocarbons derived from petrochemical routes, the LCA work related to hydrocarbons, specifically precursors for ferrocene and products formed by the Fischer-Tropsch (FT) process of chapter 6 , the use of the Finechem tool occurred (Wernet *et al.* 2009). Finechem is an open-source program running in R (Ihaka and Gentleman 1996), taking a neural network approach to estimating the impacts of specific hydrocarbons being produced via derivatives of crude oil distillation and reforming. Through user definition of the molecular properties of the investigated compound, e.g. molar weight, presence of functional groups, and other features allows the model to identify the likely impacts of its production by referencing against known substances within its database.

Since the output of Finechem was cumulative energy demand (CED) in addition to the impact assessment methodology CML 2001 (developed by the Centre of Environmental Science, Leiden University (CML) (Guinée 2001)). The approach taken with Finechem was to define a broad range of candidate proxy molecules, which were both similar to the chemical with lacking LCI data, and similar to comparable products where LCI data did exist. LCIA results were generated for the candidate products using the CED and CML 2001 methods. Therefore, it was possible to find the best representative alternatives, after adjusting for density differences, to assign an estimate impacts for the products being formed, e.g. benzene use instead of cyclopentadiene for the ferrocene precursor chemical.

3.5.4.5 Representative infrastructure inventory data

The specific tasks and approach for the capture of impacts specific to equipment used is covered where necessary throughout this thesis, but is essentially founded upon:

- equipment manuals,
- contact with equipment manufacturers,
- partial/full disassembly to gain inight into componentry parts,
- subject matter expert input

Infrastructure data is available in the accompanying appendices of this thesis

3.5.5 *LIFE CYCLE IMPACT ASSESSMENT: LIMITATIONS FOR NANOMATERIALS*

Discussed in the previous chapter in more detail was the present inability for existing LCIA methodologies to assess likely environmental and human health impacts attributable due to ENMs. In recognition of current LCIA limitations, expanding upon recommendations of (Bauer *et al.* 2008; Hischier and Walser 2012a), the presentation of LCIA results of the LCA's contained in this thesis are three-part:

1. Coverage of existing 'traditional' material impacts via the LCIA methods used.
2. Categorise and define the nanomaterials physical properties and used quantities.
3. Describe whether life cycle releases are likely and if so at what points within the life cycle.

The second and third part do not appear in the overall figures presenting LCIA results of the various studies within this thesis, however, acts as a supplementary source of qualitative information ready for when LCIA and risk assessment methodologies are in-place to better cover ENM specific impacts.

3.6 SUMMARY OF APPROACH IN ASSESSING ENMS

The LCAs conducted in this thesis all follow the same key underlying approaches. In particular with appreciation of the target audience, and the part in which the inclusion of these parties in collaborative efforts result in successful reporting and findings from studies. Through accounting for LCAs of ENMs via the approach detailed in previous sections 3.2.1-4, benefits include:

- Insight being provided to the technology developer on where largest life cycle burdens arise.
- Subject matter experts offer fresh perspectives and current thinking relevant to the emerging technology and are thus not only the prime drivers but also main benefactors of the LCA process.

- Presentation of transparent LCI data allowing further assessment once more is understood and quantified for the potential damages that ENM use and release may have on the environment and human health

- Disaggregated LCIs show separate contributors to the material impacts, allowing understanding of where their origins lie: energy, material, synthesis infrastructure. This is of use when these technologies progress to more industrial scales, and when very likely process changes occur.

3.7 APPROACH FOR PREDICTING CHANGING IMPACTS FOR SCALE-UP OF NOVEL TECHNOLOGIES

Many uncertainties and a lack of an adopted approach or methodology exist when attempting to scale the life cycle impacts of a laboratory process to larger pilot-scale and further to industrially-realised technology solutions. A precautionary approach was developed and followed within this thesis. Scale-up occurs for:

- the synthesis route of the ENM materials,

- a hypothetical plant based on an operating laboratory process.

The approach for scale-up is taken once a robust attributional LCA of the laboratory scale processes have been established, as per the approach addressed in section 3.2. Indeed, many of the practices outlined in the previous section are again used here, even if not explicitly mentioned.

3.7.1 *LEAN SETUP MODELLING*

The accurate capture of all intrinsic elements necessary for material synthesis provides the backbone of further scale-up impact predictions. Once a comprehensive insight is established for the laboratory scale process it is possible to identify areas of:

- under-utilisation of equipment

- unnecessary energy and resource use outside of direct material synthesis activities

- redundancy and combination of certain equipment pieces used

Further to these steps, the processes are modelled as continuous operation rather than individual batch synthesis. This has the effect of reducing the overall embodied impact imprinted on the materials via the used synthesis equipment. Additionally, modelling as a more continuous process has the effect of reducing aspects associated with equipment heating and cooling between synthesises.

Allocation

All of these changes occur when impacts are reported for that of a 'lean setup', to this end the laboratory equipment still remains the same, however they are being operated at, or close to, their maximum operating capabilities for the duration of their serviceable lifetimes. For example, in a traditional laboratory setup perhaps a device might be used a thousand times to conduct a 1 hour operation in its 25 year lifetime; thus per use 0.1% of equipment impact is imprinted onto the materials passing through it. However, when considering this task as part of a continuously operating system, this 1 hour operation is part of the 219,000 total hours the equipment could be used for (8760 hours per year x 25 years); thus now 0.00047 % of equipment impact is imprinted.

3.7.2 *LARGER SCALE PROCESS IMPACT FORECASTING*

The lean setup provides technology developers and other stakeholders valuable insight into the potential feasibility of the process, however. Larger scale infrastructure and process techniques will very likely be different to those of the laboratory scale, so the lean setup is only partially representative of what an industrial process or even pilot-scale process might look like. In this thesis the identification of the potential setup of a larger scale setup was beyond the scope of the work, much of this was due to uncertainties in doing so, and questions over the validity of LCAs that would be created based on predicted future systems, which have: not yet been made, where no functionally equivalent process routes were available in literature source, and where contact with industrial partners and experts in emerging-process scale-up could not be established.

Despite the limitations of the lean setup, it is decidedly useful for identifying where the inherent impacts lie, regardless of scale. Processes that are energy intense by their nature will most likely always be, and materials that do not function unless specific

precious metals or otherwise are needed will carry the impacts of using these at all deployed scales.

3.7.3 *CO-PRODUCT IMPORTANCE AT LARGER SCALE*

Laboratory scale research is primarily interested in specific mechanisms, however, co-products in the form of other chemicals and feedstocks and heats of reaction could be used when considering a larger scale setup. Examples of such important factors that may come to the fore at larger scales include:

- the use of exothermic heat of reactions for heat provision and co-generation of electricity.
- co-products formed to be considered for their potential to fulfil roles in supply chains.

3.7.4 *END-OF-LIFE ACTIVITIES*

The end-of-life treatment is an activity often over-looked when developing novel technologies, however, hypothetical E-o-L activities (based on available literature and guidance from waste treatment and disposal directives) are modelled for the different materials assessed in this thesis. Its inclusion is a necessity, and an important life cycle consideration when conducting a holistic assessment of a working technology. The materials are considered on their own merits, establishing whether:

- assess how much of initial embodied impact can be recovered / mitigated.
- precious metal recovery
- infrastructure recycling
- incineration of waste – important for 'making safe' nanomaterials , references of waste treatment issues/challenges of ENMs

3.7.5 *SUMMARY FOR FUTURE PROCESS SCALE IMPACT FORECASTING*

Many uncertainties arise when attempting to predict future impacts of any technology. These are exacerbated when dealing with emerging technologies, where their in-use

phase are not wholly proven or quantified for a working (non-laboratory) in-situ performance. Considerations regarding operatonal lifetime, degradation in performance/function.

Further uncertainties arise when considering that the technology processes for creating ENMs are themselves continually advancing and changing, a system modelled today might well be proven in the short-term to be misrepresentative of methods developed in the near-term future.

The functional properties of products formed by the ENM-incorporating solutions assessed, are proven but only currently for very small scales. Often mili-gram quantities for even extended operational times considered. Errors, experimental inaccuracies and other factors are resulting in non-exact establishment of products, are all likely to be extrapolated to very large discrepancies when the process is scaled to a more 'macro' and industrialised scale.

The many inaccuracies of scale-up require the plain statements with regard to assumptions being made to bridge models of laboratory for the representation of larger scale setups.

3.8 CO_2 CAPTURE AND UTILISATION TECHNOLOGIES; LCA APPROACH

LCA has been used in this thesis to measure carbon capture and utilisation (CCU) processes from point of CO_2 capture, until the production of carbonaceous products. To achieve this the following assessments have occurred.

Common to all processes using CO_2 as a feedstock is the need to establish:

- The impacts of capturing CO_2 (covered in the next section)

And the following steps covered in the respective process chapters (6 & 7) of this thesis:

- Resultant impacts of products formed via CO_2 conversion routes
- Net life cycle GHG impact, incurred burden of other environmental impacts
- Environmental competitiveness with the alternative/existing processes

3.8.1 *APPROACH FOR THE IMPACT OF CAPTURING CO_2*

As discussed in chapter 2, the CO_2 feedstock is most likely to come from fossil fuel plant point-source emitters in the short to medium term. This route is the most advanced to date, with various global demonstrator plants. CCU integration with such sources presents the opportunity of adding value to their waste streams whilst mitigating their net GHG emissions.

Considering a fossil fuel plant, operating without CC technology, X amount of combusted fuel releases Y amounts of CO_2. If a CC unit were to be incorporated, additional energy demands are incurred, resulting in the fuel demand rising to 'X + x', consequentially this would result in 'Y + y' CO_2 emissions. However, as reported in Odeh and Cockerill (2008), 90 % of the emissions are captured. Specific energy breakdowns are not within the scope of this assessment, however as stated by Metz *et al.* (2005) "most" of the energy requirement is for capture and compression activities, the transportation and storage activities would be the minor contributing remainder, thus the following relationship can be considered satisfactorily valid for the purposes of this thesis:

Equation 3-1 $$x = 0.9(Y+y)$$

This relationship allocates the additional fuel quantity required for CC, to the total amount of emitted CO_2 which is captured from the direct combustion of fossil fuel. There is a high sensitivity to the type of fuel being used; using UK figures (DUKES 2011) coal typically emits 0.87 kg CO_2 / kWhe , and natural gas 0.330 kg CO_2 / kWhe. In addition to direct emissions from combustion, the upstream life cycle impacts (or indirect emissions from energy use) associated with fuel acquisition play a large part in impact 'x'. This contribution is again non-fixed in its nature, and fluctuates due to a wide range of spatial and temporal factors, such as the nature; purity, difficulty of extraction, origin; efforts to reach, and transport activities. The wide range is appreciated in Figure 3-6, which is a plot of the GHG impacts pertaining to 18 coal and 14 natural gas sources across the globe as listed in Ecoinvent Database v2.2 (2010). In this thesis, CO_2 is modelled as coming from the point source emissions of a coal power plant. This is a justifiable assumption, since coal represents the largest fuel source for

UK and indeed global electricity generation, and produces CO_2 in higher flue gas concentrations than natural gas.

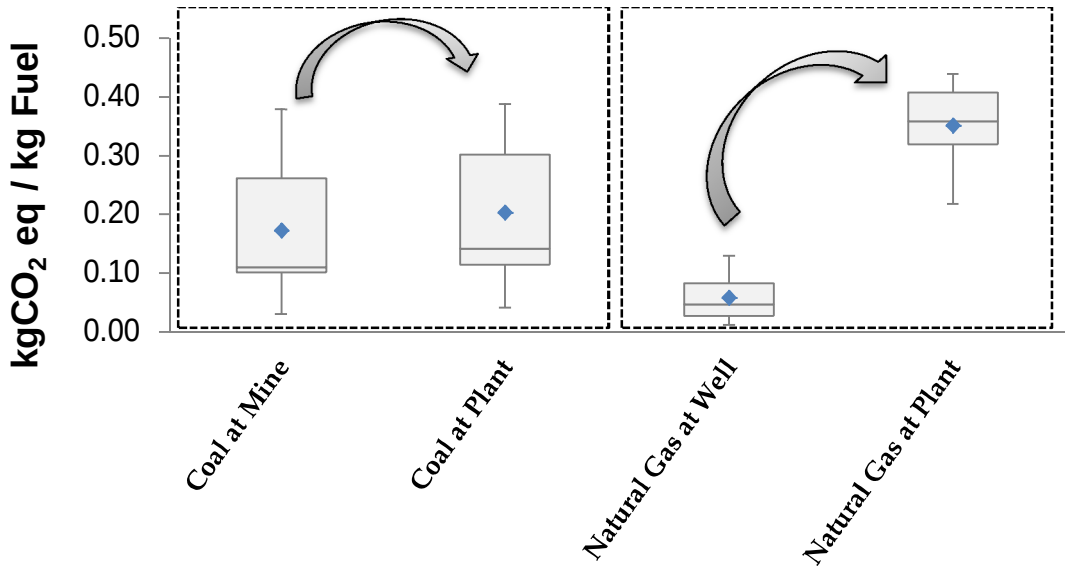


Figure 3-6 GHG emissions per kilogram, for range of coal and natural gas datasets from Ecoinvent; impacts for unit mass at extraction and distribution gates.

Ecoinvent did not have a specific UK dataset for bituminous coal generation, although it was found that few discrepancies exists between the datasets of other Western Europe datasets, thus a French dataset was used and emissions adjusted to be in-line with UK figures (DUKES 2011) of 0.87 $kgCO_2$/kWhe. The impact of increased fuel requirement is but part of the assessment, and needs consideration with the impact of additional plant infrastructure necessary to perform carbon capture. Without specific data pertaining to the latter an assumption was taken, and the additional infrastructure has been linearly scaled with the energy increase. i.e. 19 % more capital plant equipment.

Table 3-2 The environmental footprint of 1 kg of CO_2 used as a feedstock in this thesis, founded on post-combustion captured gas from pulverised coal power generators.

Impacts per captured kg of CO_2 from Pulverised Coal Power Plant		
Climate change	-8.1E-01	kg CO_2 eq
Ozone depletion	6.5E-10	kg CFC-11 eq
Human toxicity	3.7E-02	kg 1,4-DB eq
Photochemical oxidant formation	2.7E-04	kg NMVOC
Particulate matter formation	1.5E-04	kg PM10 eq
Ionising radiation	1.5E-03	kg U235 eq
Terrestrial acidification	5.2E-04	kg SO_2 eq
Freshwater eutrophication	5.9E-05	kg P eq
Marine eutrophication	1.0E-04	kg N eq
Terrestrial ecotoxicity	1.3E-06	kg 1,4-DB eq
Freshwater ecotoxicity	8.1E-04	kg 1,4-DB eq
Marine ecotoxicity	8.1E-04	kg 1,4-DB eq
Agricultural land occupation	1.0E-03	m^2a
Urban land occupation	5.2E-04	m^2a
Natural land transformation	4.6E-06	m^2
Water depletion	1.8E-04	m^3
Metal depletion	2.7E-04	kg Fe eq
Fossil depletion	2.0E-02	kg oil eq
Cumulative Energy Demand	8.8E-01	MJ

Table 3-1 demonstrates that carbon footprinting alone is not a satisfactory assessment tool, since despite net negative GHG emissions, all other impact categories are showing positive values indicating incurred impacts of various extent across the environmental impact categories assessed. These can be considered the burdens of CO_2 use as a feedstock as gather from this source. This is not intended to be a definitive CO_2 impact, since many assumptions and thus limitations in this approach are present, to eliminate or minimise these a bespoke assessment of CC technologies would yield more accurate and representative dataset. Moreover, should readers interested in the CCU technologies have more detailed datasets, either through direct involvement with CC technology researchers or in the wake of more data entering the public domain, for the impacts of capturing CO_2 they will be able to synthesise their own follow-up studies using the LCI process data contained within this thesis.

3.8.2 *MEASURING CCU FUNCTIONAL PERFORMANCE*

When assessing the different carbon capture utilisation (CCU) technologies two the functional unit is on a mass basis of the products formed. To assess the environmental footprint of these products, the embodied impact and corresponding offset impacts of the formed hydrocarbons were considered:

- $Impact\ of\ CCU\ product\ -Corresponding\ offset\ impacts$

$$If\ , > 0, then\ products\ have\ higher\ enviromental\ load$$

$$If\ , < 0, then\ products\ have\ lower\ environmental\ load$$

In the overall assessment of the GHG mitigation of the operating system is of ***one kilogram of offset CO_2 equivalent emissions***. As will be outlined in this section, this functional unit is ***not*** to be confused with:

1 kg of captured CO_2 ≠ 1 kg of converted CO_2 ≠1 kgCO_2 eq. emissions avoided

The immobilisation or diversion of CO_2 from the free atmosphere is one of two primary criteria of CCU, the other focus is the utilisation of this CO_2. To this end it is important to state that CO_2 is not the only assessed greenhouse gas (GHG) pollutant modelled within the LCA. Additionally the is inclusion of other proven GHGs gases - e.g. methane, nitrous oxides – as per the characterised values of IPCC (2007a), which affect the equivalent CO_2 emissions being offset. From the GHG-specific functional unit all other assessed environmental impacts, see Table 3-1 (page 45).

LCA strength of allowing whole life cycle consideration, taking into account where CO_2 is entering and exiting the system along its lifetime. When considering the operating performance of the system in isolation. The material, energy and infrastructure impacts are increasing the burden of the system, whilst. The immobilised CO_2 from the atmosphere, formed co-products and other recognised offsets are reducing the system's net environmental burden. The overall impact of this process is thus accountable at node 1, determining whether the process is achieving net negative impacts (the goal) or net positive. Positive burdens at node 1 indicate that the impacts of process are not GHG negative, however, this does CC not necessarily indicate an unfavourable pathway, as will be discussed next.

When expanding the assessment boundary to compare the CCU process to an existing process, node 2, it is possible to determine whether any environmental benefits are achievable. In modelling terms this equates to the avoided impacts of not extracting the equivalent hydrocarbons from traditional production routes.

Thus at node 2 it can be appreciated that a process with a negative resultant impact does not necessarily translate to the route being carbon negative. However, it is an indicator of the process being a better option compared to traditional hydrocarbons; since producing hydrocarbons by any means incurs an environmental impact.

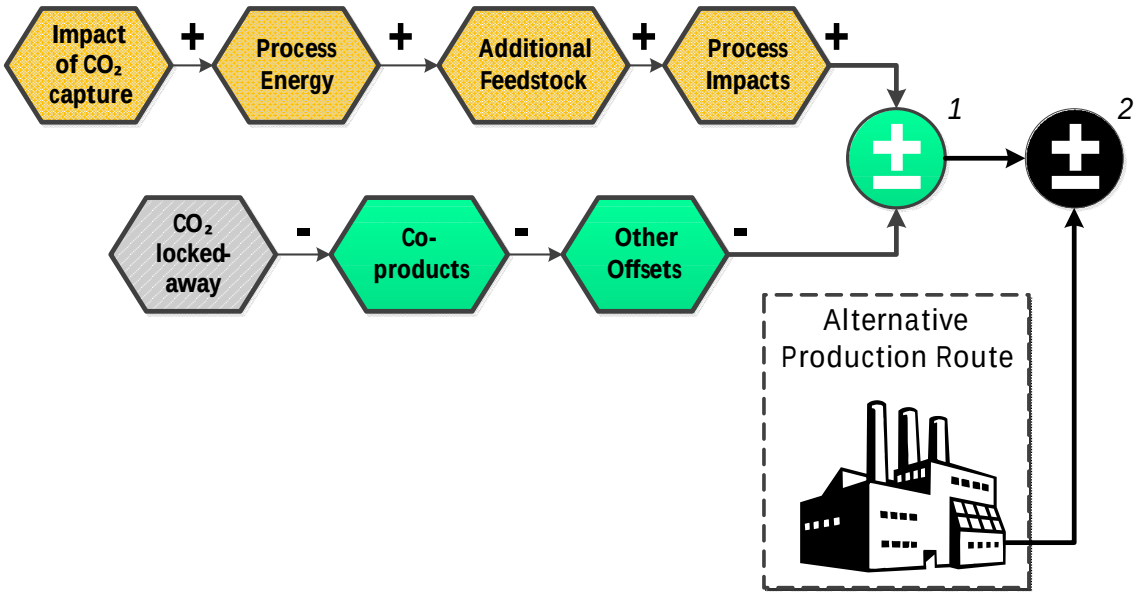


Figure 3-7 Whole life cycle considerations to point of product formation compared to existing routes.

3.8.3 *CCU PRODUCT IMPACTS*

The processes require analysis in terms of the conversion performance, CO_2 being locked-away, and subsequent selectivity towards specific hydrocarbon products, these stages are both linked and follow from one another, as shown in Figure 3-8. This is important since the overall offset will be dependent on both measures, conversion for node 1, and selectivity for node 2. Since the production of different hydrocarbons/alcohols/ and other carbonaceous compounds will each incur different environmental impacts. Amongst the converted products, a proportion of which is carbon monoxide (CO), this is an intermediately product in CO_2's conversion pathway to hydrocarbons. Thus CO production is treated as a non-waste output, as will be

addressed later in the process, with the potential for in-process reintroduction/recycling or indeed as feedstock for another auxiliary process.

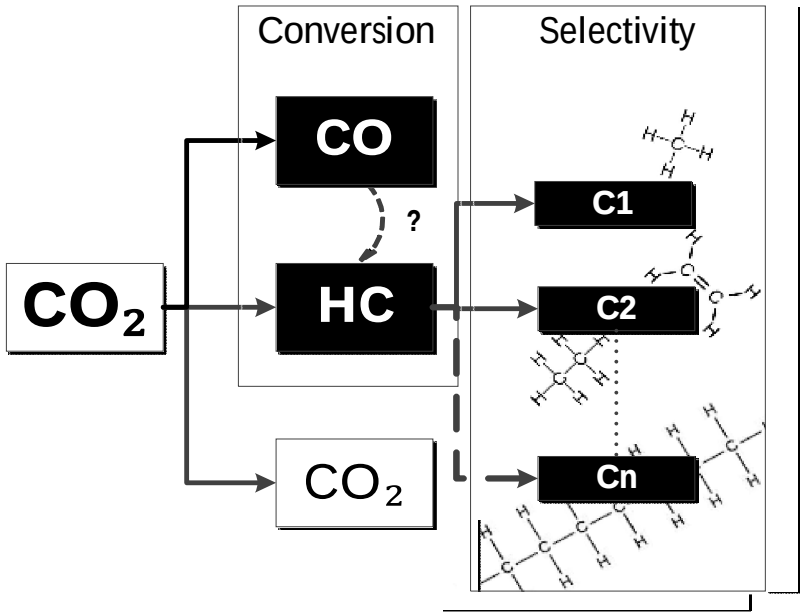


Figure 3-8 Accounting for catalyst performance. CO_2 in and out of the reactor, and on the quantity and species of hydrocarbons formed.

3.8.4 *TARGET SETTING FOR PROCESSES FEASIBILITY*

Within the scenario/sensitivity assessments of the LCA studies, process targets are set with regard to the environmental enhancement, physical performance, and operational lifetime to be met before environmental benefits are witnessed from their operation. These are informative in technology assessments, and allow other to determine if the targets are attainable based on their expertise in combating such barriers, and in deciding progressed to larger pilot-scale to industrial scale setups. A temporal metric is used, in essence the time to the 'break-even point' of the environmental impacts being measured, considering that both static and dynamic impacts are present in an operating process:

- *Static:* formed engineered nanomaterials (ENMS), and equipment infrastructure.
- *Dynamic:* feedstock use, energy demand, product and co-product formation

If a dynamic in-use offset is achieved then an opportunity to recoup initial environmental burdens of the static impacts is possible. A series of scenarios, outlined more specifically in respective assessment chapters, are taken, and broadly include the:

- process ‘as is’ with present laboratory setup and operational performances
- ‘lean’ setup, see section 3.7.1(page 57)
- comparison of materials assessed to the maximum or ‘ideal’ and maximum performance that could be expected to meet the functions.
- introduction of end-of-life recycling loops
- introduction of a renewable wind generator in place of UK grid electricity

3.9 ADDITIONAL REFERENCE DATASETS

3.9.1 *SUBSTITUTION USE OF RENEWABLE ENERGY*

In an attempt to de-couple the use of electricity with the incumbent impacts of the present UK electricity grid (see APPENDIX B: for modelled grid mix used in this thesis). The use of a European estimated wind generation source is used. This dataset is within Ecoinvent as ‘wind generation at plant’.

Wind generation is an example of a low carbon technology, expected to play a larger contributory role in future electricity grid mixes. A contrast to the current electricity mix which is set on a backdrop of predominantly fossil fuels. Appreciably the use of a 100% pure wind source is not a realistic case for sole power generation, and are thus included as indicative values of the ‘best case’ likely for the technologies, since electricity cannot come impact free.

A comparison of the modelled UK grid versus wind generation is shown in fig, it can be seen that GHG savings are appreciably received, and indeed all other impacts show similarly favourable declining burdens. However, for the case of metal depletion, wind generation is of a higher relative impact.

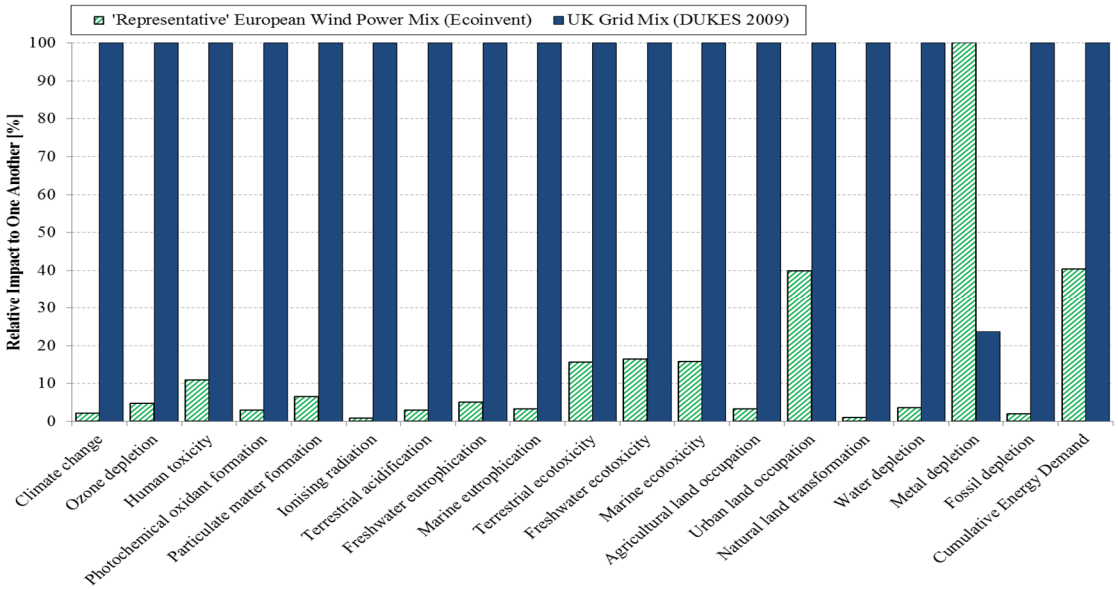


Figure 3-9 Comparing impacts between modelled UK electricity grid mix, and electricity sourced from a 'representative EU' wind power site.

3.9.2 *HYDROGEN USE*

Hydrogen is an input used in the synthesis of carbon nanotubes in Chapter 4, and in the operation of the catalysis process in chapter 6. A number of methods for hydrogen production exist from; established technologies, such as steam reforming, partial oxidation, electrolysis and biomass gasification, soon-to-be technologies; such as autothermal reforming, membrane electrolysers and ammonia reforming; towards the more experimental routes of microbial production and direct water splitting technologies via thermal and photoelectrical chemical water splitting technologies (Holladay *et al.* 2009). Although producing the same end-product, the impacts due to production of hydrogen, even via the most established production pathways differ greatly, as shown in Table 3-3.

Three datasets for hydrogen production are used in this thesis. As can be appreciated from Table 3-3Table B-5, these represent the lowest reported impact for hydrogen production from fossil fuel and renewable electrolysis routes respectively. Other practitioners using the study results within this thesis should be mindful of this choice. Although the effects of H_2 choice is measurable, they do not greatly influence the major findings and conclusions of the results detailed within this thesis. Justification for this choice is that the technologies themselves are established and commercially used

technologies. In seeking to move towards larger-scale GHG mitigating impacts of deployed CCU technologies, system feedstocks would be sourced to minimise environmental burdens.

Table 3-3 Global warming impacts of different hydrogen production routes.

Route of Hydrogen production	Specific global warming potential [$kgCO_2eq$ / kg H_2]
Natural gas reformation	**~ 7.8 (Plastics Europe 2011)** **~ 11.0 (Koroneos *et al.* 2004)** **~ 8.9 (Ruether *et al.* 2005)**
Coal gasification	**~ 12.4 (Ruether *et al.* 2005)**
Fossil fuel cracking	**~ 1.7‡ (Plastics Europe 2011)**
Electrolysis	**~ 1.0‡ (Plastics Europe 2011)**
Electrolysis via renewables	**~ 0.8 (Koroneos *et al.* 2004)** **~ 0.2‡ (adapted from Plastics Europe (2011))**
	‡ datasets used in this thesis.

In the Appendix B.2, information is given for the hydrogen dataset. Including the trade-offs between hydrogen sources. Whereas a 100% electrolysis route of H_2 production is modelled as to de-couple this feedstock from fossil fuel origins, and thus associated GHG, fossil fuel reserves, and cumulative energy demand, it can be seen that other impacts are indeed greater for the chosen electrolysis-H_2.

The choice of this particular electrochemical membrane cell was made in the vision of using sea water, with the sodium chloride within it the necessary electrolyte. The co-products of chlorine and sodium hydroxide are non-trivial in terms of industrial application, and thus piggy-backing off these would allow for additional economic drivers in place of an electrolysis route which supplied hydrogen and oxygen alone from a cell requiring other electrolytes, such as potassium based. Furthermore, the chlorine industry in Europe is actively seeking ways to use this 'unneeded' hydrogen by-product from their industry(Euro Chlor 2011). This use of hydrogen viewed as a waste source, is in the similar vein to CO_2 use.

3.10 SUMMARY

This chapter has detailed the:

- reference inventory datasets used,
- life cycle impact assessment (LCIA) methodologies.
- over-arching purpose and approach to assessing the different functions of the systems assessed in this thesis.
- and the core datasets referenced by the majority of operating systems covered.

Chapter 4: LCA OF FORMING MULTI-WALLED CARBON NANOTUBES

: AND THEIR PREPARATION FOR CO_2 CATALYSIS

Within this chapter is LCA work related to the formation of Multi-Walled Carbon Nanotubes (MWCNTs) *via* a Chemical Vapour Deposition (CVD) synthesis route.

- A laboratory scale CVD synthesis route, along with comprehensive life cycle inventory data for the MWCNT growth is reported in detail.
- LCA work is cradle-to-grave (negating a use phase which is covered in chapter 6) concerned with the growth and end-of-life incineration of the grown MWCNT.
- Highest life cycle impacts (from high to low) were due to the use of the furnace, specifically the energy usage during growth and incineration, and of the embodied impacts of the furnace infrastructure itself.
- The gases involved had an imprint on the LCIA results, however, these were comparatively small, and smaller still were the impacts due to auxiliary equipment and the use of MWCNT feedstock, catalyst and other chemicals.
- Through sensitivity analysis it is shown that MWCNTs grown *via* a similar process could be 10% of the impacts currently measured.
- Prepared MWCNTs have many potential applications, in this chapter thesis their usage as catalysis were investigated. A novel approach of activating the iron left over in the initial synthesis of the nanotubes (often considered a material impurity) is found to be far less impactful than a previous route used. Indicating benefits of knowing the application of the engineered nanomaterial, tailoring the process to reduce unnecessary stages.

Journal article related to this work: *Griffiths, O. G., J. P. O'Byrne, L. Torrente-Murciano, M. D. Jones, D. Mattia and M. C. McManus (2013). "Identifying the largest environmental life cycle impacts during carbon nanotube synthesis via chemical vapour deposition." Journal of Cleaner Production **42**: 180-189.* (Griffiths et al. 2013a)

4.1 CARBON NANOTUBES: BRIEF STATUS AND INTRODUCTION

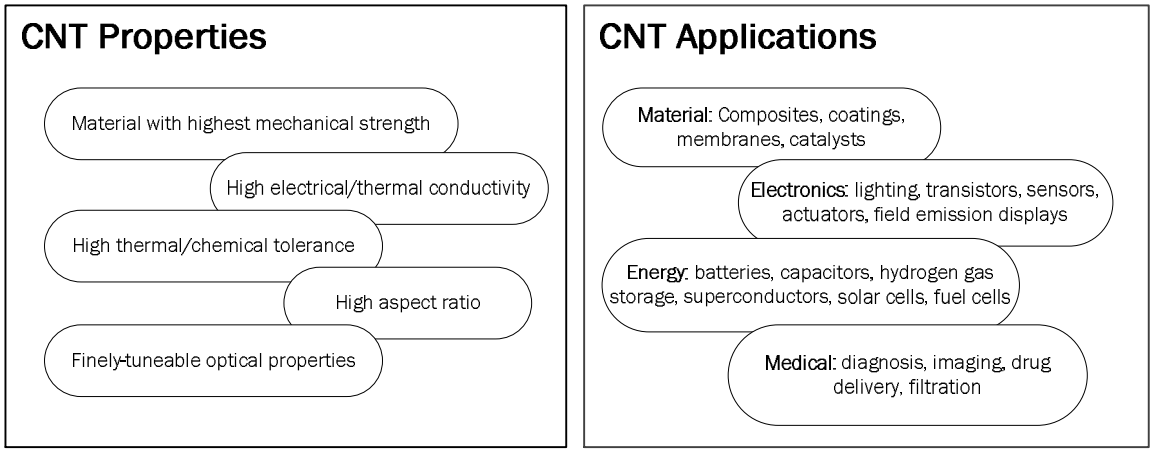


Figure 4-1 Carbon nanotube (CNT) and some identified properties and applications.

Since the discovery of carbon nanotubes (CNT) in the early 1990's (Iijima 1991), the whole field of nanotechnology has become increasingly aware of the new and exciting prospects offered from this material and its derivatives (Lines 2008; Dahlben and Isaacs 2009). CNTs are arguably the most discussed of all ENMs with the list of properties and already commercial applications ever-increasing; a snapshot is shown in Figure 4-1. However, in contrast to the growth of applications see concerning the potential uses of CNTs, there is little certainty regarding the potential widespread environmental impacts of their industrial-scale deployment (Singh *et al.* 2008; Upadhyayula *et al.* 2012). This gulf is exemplified in a survey result of published academic publications Figure 4-2.

The nature of the integration, use, and environments in which CNTs are likely to encounter are vast, presenting a challenge to anticipating where likely impacts may occur (Köhler *et al.* 2008; Eckelman *et al.* 2012), this thesis seeks to contribute to a wider appreciation of CNT life cycle imapcts.

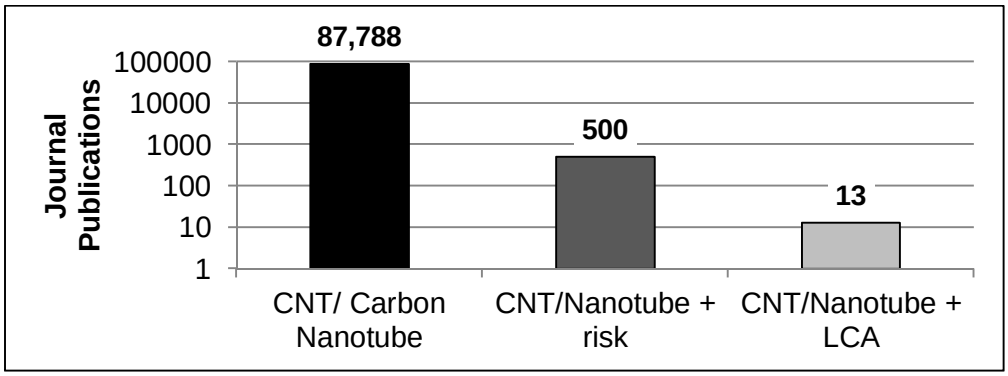


Figure 4-2 Web of science results filtered for publications on CNTs.

4.1.1 *CNT* PRODUCTION ROUTE COVERED IN THIS CHAPTER

Whilst conducting a literature review and search of CNT assessments (see chapter 2) it became apparent that previous LCA work would not be directly applicable for the application to hand. Uncertainty over the actual characterised CNT being formed in other studies was a concern when discussing with the specific technology developers; since the specific material properties are demanded for the catalysis application are dependent on the synthesis and material handling pathways. Furthermore, many other study results were incomplete in terms of actual coverage of system flows, and in accounting for wider environmental impacts, more detail was required to appreciate discernable process activities and their contributing impacts in forming usable materials.

This thesis is focused on multi-walled carbon nanotubes (MWCNTs), synthesised *via* a laboratory scale chemical vapour deposition (CVD) synthesis pathway. CVD is amongst the three predominant (Healy *et al.* 2008) methods of CNT synthesis, together with arc ablation (arc) and high pressure carbon monoxide (HiPCO) routes. CVD growth of CNTs is the most likely method for industrial growth of nanotubes (Kushnir and Sandén 2008; Zhang *et al.* 2011) given that the process occurs at ambient pressures and at lower temperatures than other cited synthesis routes (Guo *et al.* 1995; Keidar and Waas 2004; Ortega-Cervantez *et al.* 2005) and is more precise and versatile in terms of CNT formation and properties (Zhang *et al.* 2011).

Focusing on this CVD pathway in detail will be a sound stepping stone in appreciating life cycle burdens of the CNT material class as a whole. Industrial routes with multi-tonne CNT production capabilities are needed and under-development to satisfy the ever growing consumer demand. LCA work is a key tool when working towards selecting and guiding the advancement of cleaner industrial synthesis pathways.

4.1.2 *LCA WORK CURRENTLY IN THE FIELD OF CNTS*

LCA is a well placed tool for the holistic assessment of CNTs and their potential penetration and substitution with existing materials within the marketplace. To date LCAs and related analysis have uncovered a great deal regarding their potential impacts in servicing different applications. Major findings have identified CNTs as

energy-intensive materials (Healy *et al.* 2008; Ganter *et al.* 2009; Upadhyayula *et al.* 2012), offsetting these high embodied impacts is found to be dependent on in-use operation (Bauer *et al.* 2008). However, few studies have considered a holistic CNT life cycle, and a recent review by Upadhyayula and colleagues (Upadhyayula *et al.* 2012)of LCAs of CNTs concluded that gaps still exist in this field. Many of these gaps are present for the accurate accounting of the synthesis of CNTs, a necessary area when attempting to measure any life cycle impacts of a material.

4.1.3 *LCA CONTRIBUTION OF THIS WORK IN CNT FIELD*

The LCA work and findings contained in this chapter, builds on missing gaps, or weaker areas of scientific understanding, concerning:

- The impacts of all precursor chemicals and materials required for a MWCNT synthesis route.
- A complete LCA, covering all necessary resource, energy, and equipment usage.
- Characterised waste streams are presented.
- Results are in context for a characterised CNT product.
- Additional analysis for parallel processes preparing a CNT product for a specific application.
- Insight into likely impact reduction, through enhanced process, and lower impact CNT synthesis.
- Work is transparently reported, available to others seeking to use it in the wider field of LCA.

4.2 Assessing The MWCNT CVD Batch Synthesis Route

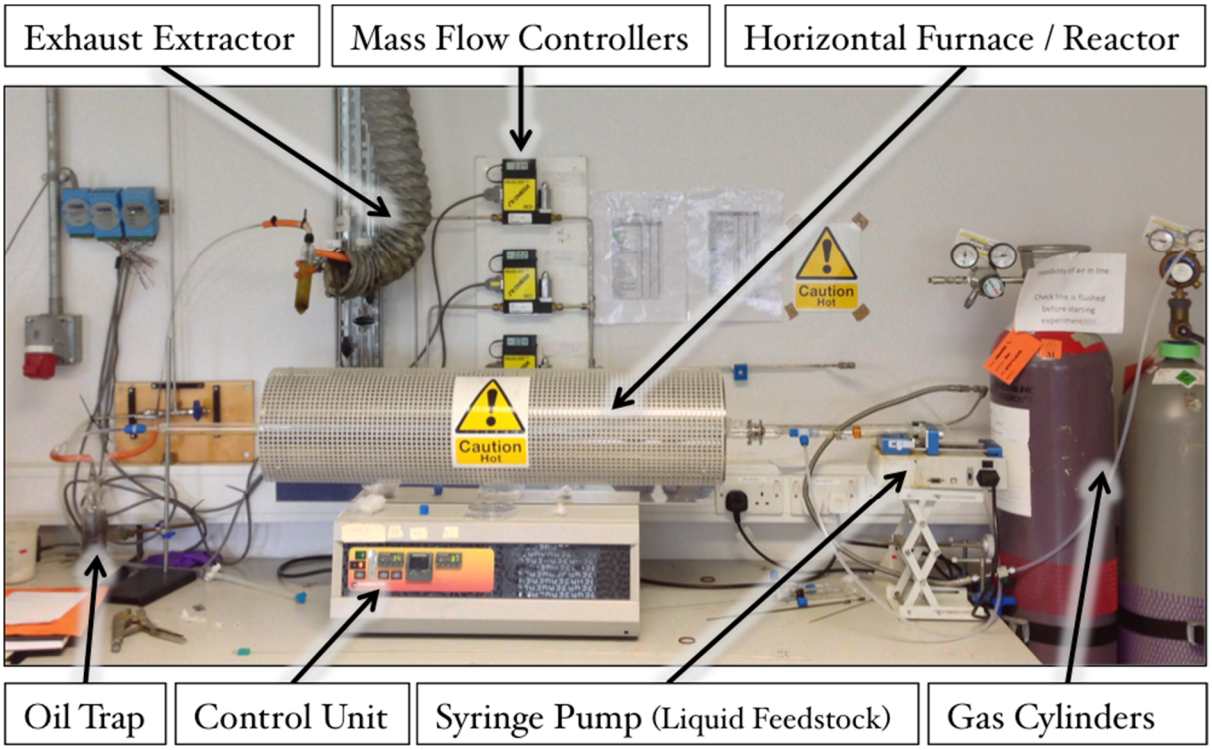


Figure 4-3 The laboratory setup for the synthesis of MWCNT.

The MWCNTs are grown within a horizontal furnace reactor; the laboratory setup is shown in Figure 4-3. The process occurs at elevated temperatures of 790 °C, forming from the injection of a mixture of hydrocarbon feedstock and an iron-based catalyst; 0.20 g of ferrocene dissolved in 10 ml of toluene. Ferrocene decomposes releasing elemental iron which catalyses the reaction between the carbon-feedstock, toluene, and hydrogen gas. The carrier gas used is argon (Ar), ensuring free of oxygen and water vapour and provides the flow required to carry the reactants into the furnace reaction chamber. Taking no part in the reaction Ar's secondary function is to ensure controlled heating and cooling of the furnace thus preventing equipment damage.

The MWCNTs propagate on the surfaces within the reaction chamber, a quartz tube located axially within the heating walls of the furnace. Placing a substrate within the quartz tube, allows the deposited MWCNTs to be readily-removable and in a useable form for subsequent handling and processing. Suitable substrates (not including the quartz tube) for MWCNTs were carbon monolith materials and crystalline silica. Once cooled, under a protective argon atmosphere, the MWCNT is removed from the furnace.

4.2.1 *MWCNT CVD GROWTH PROCESS MODELLING ASSUMPTIONS*

Table 4-1: Stages involved in the CVD of MWCNTs

Stage	Description
1	**A preparatory process for the catalyst (ferrocene) and carbon feedstock (toluene).**
2	**The heating of the furnace, under protective argon carrier gas.**
3	**Growth period of MWCNT: Once the furnace reaches 790 °C, the injection of catalyst and carbon feedstock at a rate of 10 ml/h occurs within a 50 standard cubic centimetres per minute (sccm) flow of H_2 and 450 sccm flow of Ar.**
4	**Controlled cooling of furnace to prevent thermal oxidation of MWCNT. Argon can be turned off below ~300 °C due to the carbon nanotubes' stability in air below this temperature**

MWCNT growth stages *via* chemical vapour deposition can be split into 4 distinguishable stages, as defined in The MWCNTs are grown within a horizontal furnace reactor; the laboratory setup is shown in Figure 4-3. The process occurs at elevated temperatures of 790 °C, forming from the injection of a mixture of hydrocarbon feedstock and an iron-based catalyst; 0.20 g of ferrocene dissolved in 10 ml of toluene. Ferrocene decomposes releasing elemental iron which catalyses the reaction between the carbon-feedstock, toluene, and hydrogen gas. The carrier gas used is argon (Ar), ensuring free of oxygen and water vapour and provides the flow required to carry the reactants into the furnace reaction chamber. Taking no part in the reaction Ar's secondary function is to ensure controlled heating and cooling of the furnace thus preventing equipment damage.

The MWCNTs propagate on the surfaces within the reaction chamber, a quartz tube located axially within the heating walls of the furnace. Placing a substrate within the quartz tube, allows the deposited MWCNTs to be readily-removable and in a useable form for subsequent handling and processing. Suitable substrates (not including the quartz tube) for MWCNTs were carbon monolith materials and crystalline silica. Once cooled, under a protective argon atmosphere, the MWCNT is removed from the furnace.

Once grown, further processing stages for the MWCNTs are specific to the intended application of the material. However, a purification stage is often undertaken post MWCNT growth, whereby the material is treated to remove any soot, debris and any

other impurities such as the elemental iron present in the catalytic growth of the nanotubes. A single step acid treatment is modelled in this LCA work, providing an indicative account in the context of the whole life cycle of MWCNT synthesis.

Material estimates for the major components within the tube furnace have been used, along with the assumption that 2 batches per day are attainable, giving an annual production of 500 batches, across an expected serviceable life of 30 years. The quartz tube, situated inside the furnace during growth, has been modelled from a dataset covering the production of glass tubes within Ecoinvent. The tube is considered as part of the furnace infrastructure since it largely re-used per synthesis. Electricity consumption is measured directly as the furnace is heated at a rate of 5 °C/min until reaching the reaction temperature of 790 °C. Throughout the furnace heating period Ar gas is introduced *via* a mass flow controller (MFC), estimated serviceable life of MFC is 10 years.

Once the temperature reaches 790 °C, it is held for 1 hour, during this period argon flow is increased and a second mass flow controller is used to introduce H_2. The ferrocene-toluene (MWCNT catalyst-feedstock) is injected concurrently, once at reaction conditions, at a rate of 10 ml/hr *via* a mechanical syringe pump.

4.2.2 *GOAL AND SCOPE OF LCA STUDY*

In the wake of initial LCA studies on the topic of CNT synthesis it is apparent that inventory and process detail is an area in need of addressing, especially pertaining to the synthesis infrastructure and upstream chemicals and feedstocks use. This LCA work defines all process flows, and assesses their relative contribution towards the environmental impact of forming MWCNTs.

The MWCNT material can be appreciated as having a range of applications, in this case they are destined for use as catalysts[4] utilising active iron nanoparticles. In the latter parts of this chapter (section 5), LCA will be used to compare two processes for preparing MWCNTs for use as catalysts. The latter catalyst preparation route being a novel approach which incorporates the active material during MWCNT growth, as

[4] Specifically the Fischer-Tropsch coupled reverse water-gas shift reaction (FT-RWGS), see chapter 6.

opposed to (a more typical) process of introducing the active catalyst material onto the MWCNT surface later.

An additional goal will be to model the MWCNT CVD process as it moves from the current laboratory 'batch scale' towards a more streamlined route akin to a potential industrial process. Using LCA results as the focus for process improvement, the least environmentally impactful route of producing the MWCNT material *via* a 'lean' laboratory setup (within the bounds of applicable and realistic process projections and assumptions) is investigated.

4.2.3 *MEETING THESIS OBJECTIVES*

Objective 1. Establish the environmental impacts of forming the nanomaterials

Objective 4. Communicate to technology developers key life cycle results for action

Objective 5. Communicate wide environmental impacts

4.2.4 *SYSTEM BOUNDARY FOR LCA*

The impact of forming MWCNT will be assessed on a cradle-to-production gate basis, as per the laboratory setup investigated. The system boundary used for the LCA is shown in Figure 4-4, this ring-fence encompasses all distinguishable upstream material and energy flows for the chemical reactants, energy use, laboratory infrastructure and generated waste emissions associated with the MWCNT CVD growth process.

Transport activities for upstream process inputs are included, as per the data provided within the used datasets of Ecoinvent (Althaus H.-J. 2007), however, transport stages between the specific manufacturing plants and the laboratory have been negated due to uncertainties regarding modes of transport and distances travelled. These omitted life cycle activities would foreseeably add very little to the overall impact due to transport being nearly always a minor contributor to the overall environmental impact of a fine chemical production Wernet *et al.* (2010). However, future studies would be recommended to include transport activities once likely production lines become more known and established.

The system boundary is expanded upon in chapter 6 of this thesis to cover an in-use, catalysis application. Additionally a hypothetical end-of-life material incineration / disposal process is explored in section 3.3, to provide life cycle impact context to such an activity.

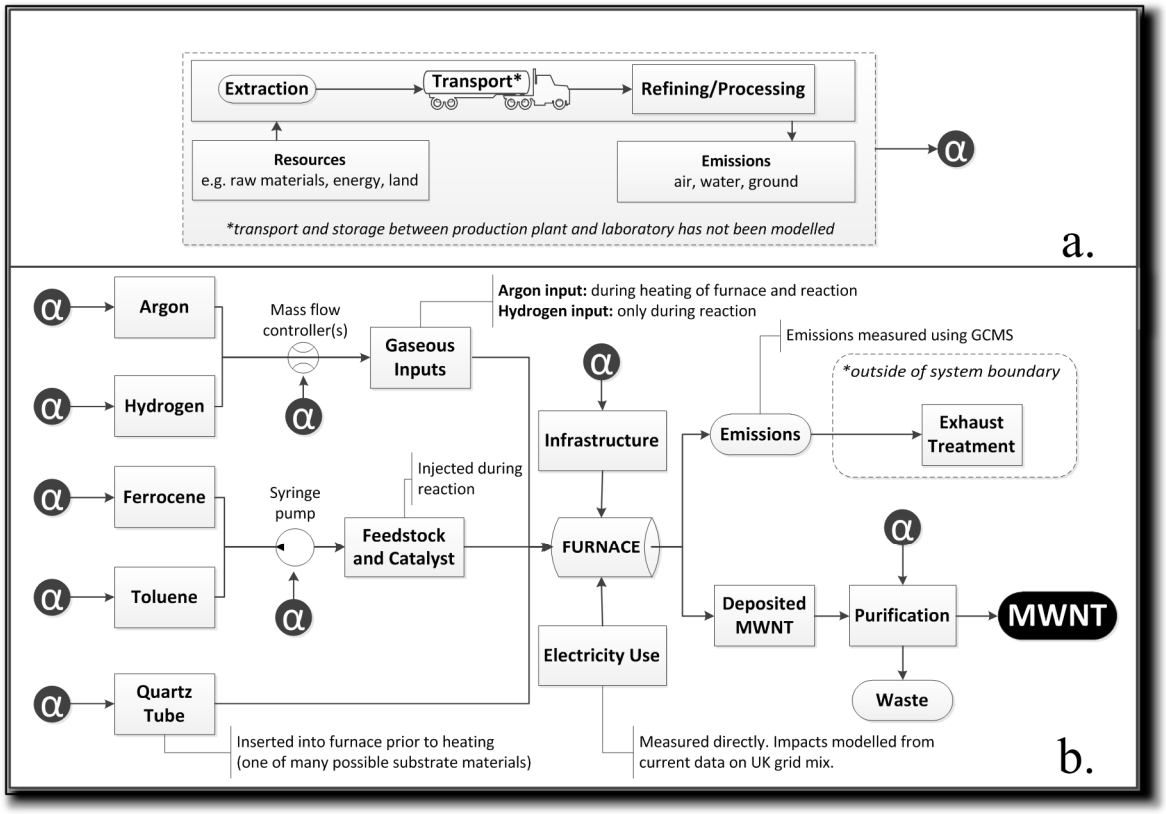


Figure 4-4 : (a) The system boundary for the precursor steps in the formation of the chemical/materials used, (b) The system boundary of the MWCNT product grown *via* the laboratory scale CVD process.

4.2.5 *FUNCTIONAL UNIT FOR MWCNT SYNTHESIS*

The LCA functional unit, to which all environmental impacts relate, will be for a typical laboratory 'batch' of the MWCNTs grown *via* the CVD process. Relating impacts on a per batch basis is more instructive for technology developers involved in CNT synthesis than the fixing of the functional unit to a particular yield of product. The batches of grown MWCNT typically consist of ~**0.3 g of retrievable and usable product**.

4.2.5.1 MWCNT process yield

In order for this synthesis route to be compared to other and future MWCNT synthesis routes the process yield is given relative to this functional unit. This batch synthesis

represents a 355 wt. % product yield. This yield calculation is used by others in the field of MWCNT growth (Louis *et al.* 2005), which relates the catalyst used for the obtained nanotube product.

Equation 4-1

$$MWNT\ yield\ (wt.\%) = \frac{obtained\ MWNT\ mass - catalyst\ mass\ after\ reduction}{catalyst\ mass\ after\ reduction} \times 100$$

The catalyst mass reduced is the 0.066 g of iron present within the 0.2g ferrocene catalyst injected into the reactor. Relating this mass of iron to the 0.3 g of obtained nanotubes provides the 355 wt.% value.

4.3 LIFE CYCLE INVENTORY DATA FOR MWCNT GROWTH

A key contribution of the work outlined within this thesis is the depth and detail of the LCI data established. The LCI work for MWCNT growth captures the chemical building-block constituents of the nanotubes, the energy consumed necessary for achieving reaction temperatures and operating auxiliary control equipment. The capture of inventory impacts, as per the system boundary shown in Figure 4-5 and the specific input and output flows defined in Figure 4-5. Direct measurements are made for the:

- feedstock, reactants and other chemical flows,
- electricity consumed by the different equipment, and
- dimensions, masses, constituent parts of the MWCNT synthesis apparatus.

Relevant details of the inventory data used in this LCA case study are stated within this chapter. Fully listed inventory datasets are available in the accompanying Appendix C.3.

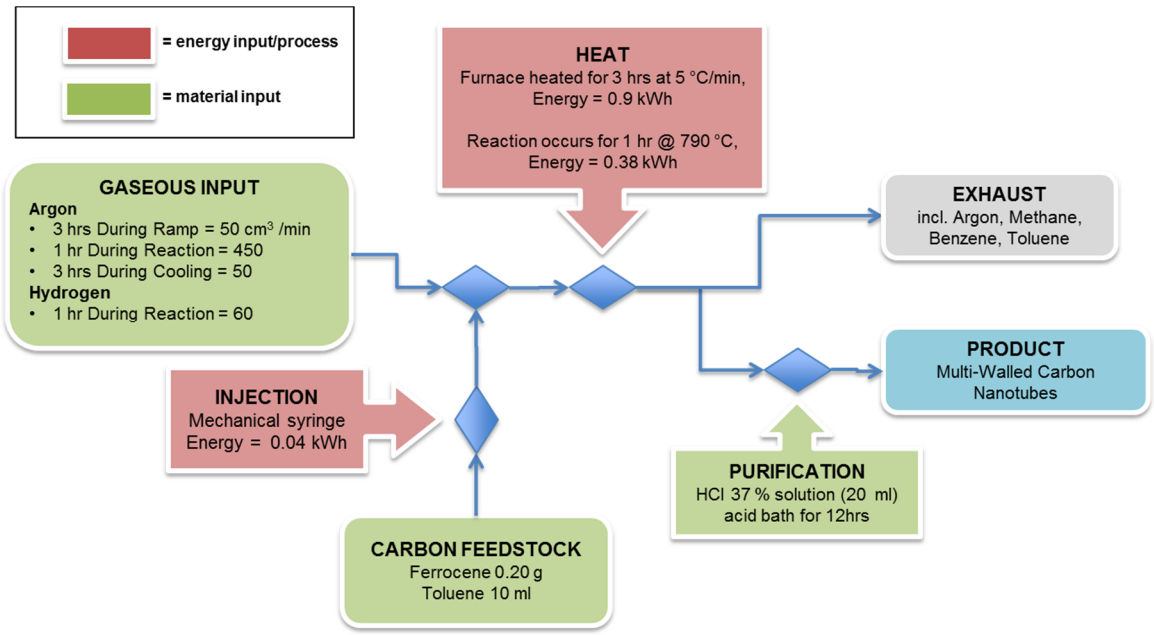


Figure 4-5 Energy and material flows into the batch production of MWCNTs

4.3.1 *CHARACTERISED DETAILS OF THE FORMED MWCNTS*

Through the use of electron microscopy techniques the size, structure and nature of the formed MWCNTs were characterised. In the anticipation of impact assessment methodologies for engineered nanomaterial release, fate and exposure within the biosphere, the characterised details pertinent for supplementary consideration are as follows:

- Maximum potential release to air/water/land sources = 300 mg.
- Wall thickness ranging from 40 – 60 nm, and tube lengths in the region of 10 µm.
- In a fibrous, high aspect-ratio structure up to 250.
- Trace quantities of nano-iron particles with minimum dimensions of a few nanometers.
- Due to the nature of the catalysis application there is very little chance of MWCNT release during use, however, production and end-of-life activities are potential exposure pathways.

It is believed that this information along with the accompanying tunnelling electron microscope (TEM) images of Figure 4-6, will be sufficient when risk assessment / LCA practices are sufficiently developed to account for nano-born impacts. The left image

shows the hair-like cluster of MWCNTs, and right shows an individual nanotube, axially viewed, with multi-walled structure, circa ~13 walls.

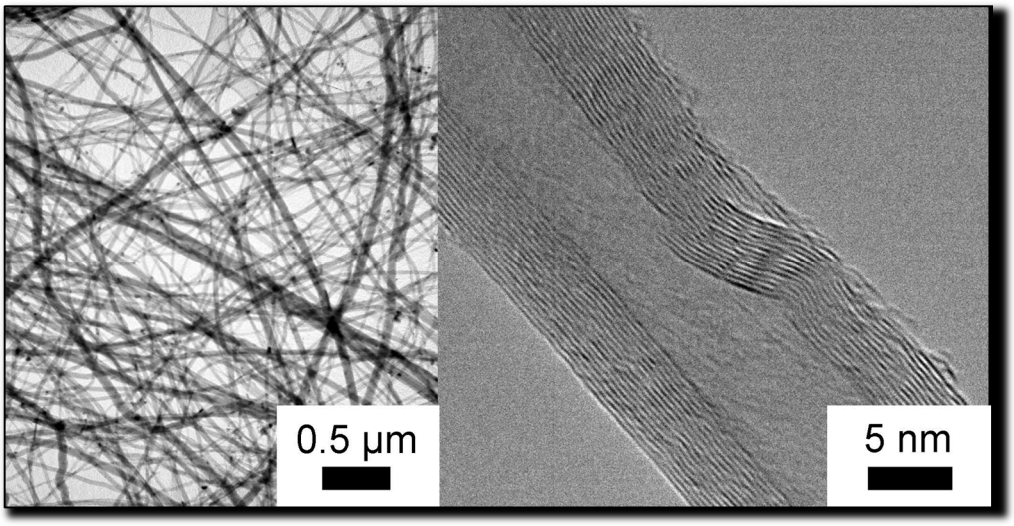


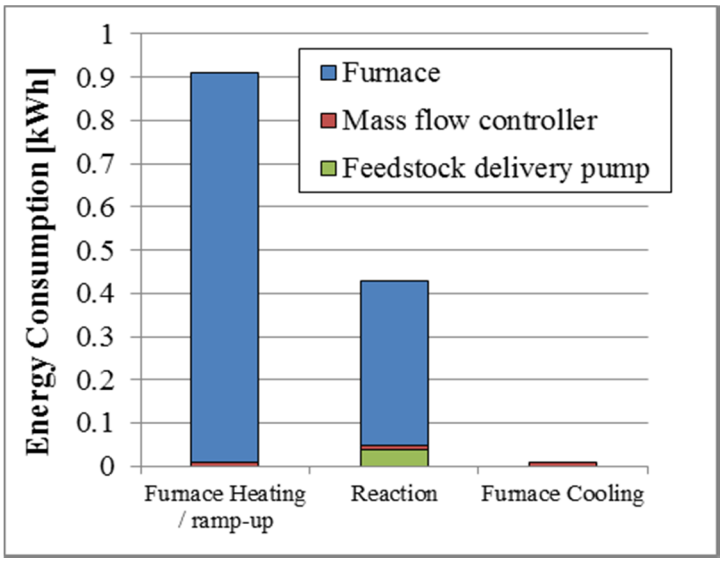
Figure 4-6: Transmission electron microscope (TEM) images of the MWCNTs assessed in the related LCAs of this thesis.

4.3.2 *ELECTRICITY CONSUMPTION*

The amount of energy consumed by the electrical equipment was measured using an in-line power meter. The horizontal reactor furnace draws power during the ramp-up period as the temperature ascends from ambient to 790 °C, subsequent power is consumed to maintain the reaction chamber at this elevated temperature during the MWCNT growth period. One or more of the mass flow controllers, responsible for argon and hydrogen gas flows, are active during the furnace ramp-up, reaction and cooling periods of the process. A pump injects the feedstock-catalyst solution into the reactor *via* an electrical stepper motor. The respective energy demands were measured across repeated runs and are shown in Table 4-2, the recorded values fluctuated ± 5 %, however the accuracy of the power meter used lies within this range. The MFC drew an immeasurably small quantity of electricity during the synthesis of 1 batch of MWCNT, its consumption was calculated theoretically and verified with the power meter for extended operating run times.

Table 4-2: The measured energy consumption of the laboratory equipment, kWh.

	Furnace Heating / ramp-up	Reaction	Furnace Cooling
Furnace	**0.9**	**0.38**	**N/A**
Mass flow controller	**0.009 (1 unit for 3 h)**	**0.006 (2 units for 1 h)**	**0.009 (1 unit for 3 h)**
Feedstock pump	**N/A**	**0.04**	**N/A**



4.3.3 *CHEMICAL AND MATERIAL INPUTS*

All chemical quantities are based on material properties at standard temperature of 20 °C and ambient pressure of one atmosphere. The corresponding mass quantities are the input values used for accounting their respective life cycle burdens.

Table 4-3 Chemical usage in the CVD growth of MWCNTs (‡ Ecoinvent Database v2.2 (2010))

Chemical	Use	Quantity (g)	LCI Data Used
Argon	**Reaction carrier gas**	**Ramp-up: 14.7** **Reaction: 44.1** **Cooling: 14.7**	**Argon, liquid, at plant ‡**
Hydrogen	**Reactant**	**0.25**	**Hydrogen, liquid, at plant ‡**
Toluene	**Reactant**	**8.67**	**Toluene, liquid, at plant ‡**
Ferrocene	**Catalyst**	**0.20**	**Own data (see APPENDIX D:) ‡**
HCl acid	**Purification**	**23.7**	**HCl acid, Mannheim process, at plant ‡**

4.3.4 *WASTE STREAMS AND EMISSIONS*

The relation of directly measured and characterised emission streams from carbon nanotube synthesis is missing in the LCA field on the topic (Upadhyayula *et al.* 2012). For this process direct gaseous samples of the exhaust emissions were taken during the MWCNT growth period, and a cold trap was used to condense exhaust flow over the entirety of the reaction period. The respective samples were analysed using gas chromatography mass spectrometry (GCMS) and flame ionisation detection (FID) techniques.

Additionally to airborne gaseous emissions, waste from this process comes as deposited carbon soot inside the walls of the reaction chamber; there are potential trace quantities of carbon nanotubes and particulates as part of this.

Table 4-4 Exhaust gas composition during one batch growth of MWCNT

Exhaust gas species	% of exhaust	Quantity
Methane	**11.0**	**0.41 g**
Benzene	**12.2**	**0.50 g**
Toluene	**76.8**	**3.01 g**

4.3.5 *INFRASTRUCTURE*

The infrastructure involved in CVD synthesis of MWCNT, see Figure 4-3, can be regarded as broadly conventional in terms of componentry parts, but specialist in their configuration as electronic devices, thus specific inventory data was formulated. The capture of inventory data for the equipment was two-pronged combining direct measurements-through full or partial disassembly- of the unit; physical size, masses, material identification, and combining these with manufacturer equipment manuals for confirmation of specific details. (Carbolite 2011; Harvard Apparatus 2011; Omega Engineering Inc. 2011).

With the use of peer-reviewed Ecoinvent Database v2.2 (2010) material inventory datasets, representative of the metals, plastics, electronic parts and other sub-components incorporated in the construction of the equipment are chronicled. The

resultant lists of sub-components are broken down into mass quantities used in the inventory reporting for the LCI process.

Table 4-5 Source of inventory for infrastructure

Device	Inventory Data Source
Furnace Controller Unit	**(Carbolite 2011)**
Mass Flow Controller	**(Omega Engineering Inc. 2011)**
Feedstock Pump	**(Harvard Apparatus 2011)**

4.3.6 *INVENTORY CONTRIBUTIONS TO THE FUNCTIONAL UNIT*

Once LCI accounts of the equipment and componentry parts were established, the allocation of these life cycle burdens to the obtained MWCNT product was performed. In accordance to the amount of MWCNTs that could be realistically grown via this method and with the equipment assessed, the percentage allocation of the embodied impacts of infrastructure per batch growth is stated in Table 4-6

Table 4-6 Allocation of total infrastructure life cycle impacts per batch of MWCNT formed

Equipment	Lifetime Years	Allocation per batch of MWCNT %
Furnace	**30**	**~ 0.0067 %**
Mechanical syringe pump	**10**	**~ 0.02 %**
2 x Mass flow controllers	**10**	**~ 0.04 %**
Common assumptions: 2 batches per day, 5 days per week, 50 weeks per year » Allocation $\approx \frac{1}{2 \times 5 \times 50 \times Lifetime} \times 100$		

Effort was taken to capture an accurate account of infrastructure componentry parts, in particularly the electronic components which were found to be especially influential on environmental impacts; these are reported in full in the accompanying Appendix C.3 of this chapter.

4.4 LIFE CYCLE IMPACT ASSESSMENT

4.4.1 *LCIA METHODOLOGY*

The ReCiPe midpoint (Goedkoop M.J. *et al.* 2008) and cumulative energy demand (CED) methodologies were employed in the assessment of life cycle impacts of MWCNT growth.

4.4.2 *LCIA RESULTS*

The impact of a single batch of grown MWCNTs, is presented in Figure 4-7 and shows the impacts across all 18 ReCiPe midpoint categories. Figure 4-7 presents normalised and not characterised midpoint values, these have been used to better graphically represent the relative impacts across different life cycle stages and between activities, a full characterised dataset is presented in Appendix C.2.

The axis values refer to a normalised score, calculated by comparing the respective life cycle impacts of the system under investigation, with the average annual per capita impact, in this case for the European population. For example, looking at the "Exhaust Emissions" impact during the MWCNT growth phase, the value reported for the impact category *"Photochemical oxidant formation"* is 3×10^{-4}, or 0.03% of the annual impact for a typical EU citizen in that particular category. Similarly during the furnace heating period, a footprint equivalent to 0.07% of an average EU citizen's annual detrimental impact on natural land transformation.

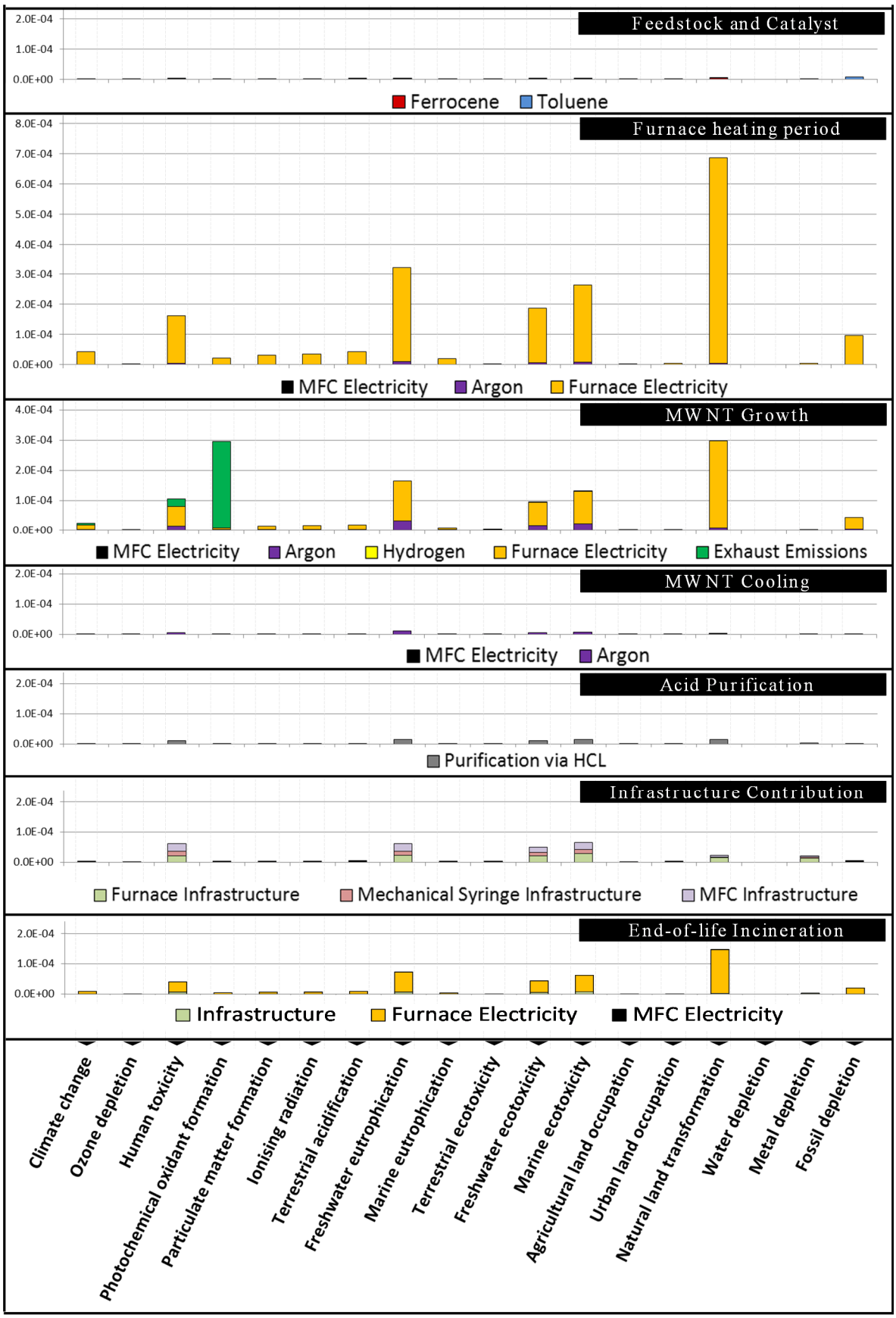


Figure 4-7:Normalised life cycle impact assessment of the MWCNT synthesis

4.4.3 *ELECTRICITY USAGE LCIA*

The dominant life cycle stage in the whole context of MWCNT growth are the impacts associated with the heating period of the furnace. The omni-dominant contributors to furnace heating impacts are those associated with the electricity requirement in reaching the reaction temperature conditions. The second largest impactful life cycle stage is during MWCNT growth, again furnace electricity requirement the major contributor. The impacts of electricity usage, as stated in chapter 2, lay upstream in the extraction of the primary energy reserves and the generation and distribution impacts of the formed electricity.

4.4.4 *GASEOUS EMISSION IMPACTS*

During the growth phase, the generated exhaust emission impacts are modelled as the direct release of the gaseous hydrocarbons; detailed in section Overall exhaust gases have a minor contribution across the majority of impact categories. However, the volatile organic compounds (VOCs) present in the form of benzene and toluene, give rise to a more measurable contribution to the whole system's human toxicity effects, and a very high formation of photochemical oxidants; responsible for ground-level ozone formation; an impact with damaging effects (potentially fatal) on the respiratory system (EPA 2013) and effects on vegetation and crop-growth (Davison and Barnes 1998; Ashmore 2002). The small proportion of methane present in the exhaust emissions can be appreciated as being a direct GHG release from the process, and is shown to be a contributor in the overall climate change impacts, both during growth and across the whole life cycle assessed.

The direct release of exhaust emissions would not be permitted within a regulated industrialised process. Therefore, these impacts are presented as reasons for the development of a suitable extraction and treatment system to prevent these emitted impacts. The inclusion of an exhaust stream waste treatment process would incur additional life cycle burdens, although anticipated to be of little impact, would require further inventory capture in subsequent LCAs of a potential future system.

4.4.5 *CONTRIBUTING IMPACTS FROM LABORATORY INFRASTRUCTURE*

After electricity consumption, the environmental implications of the laboratory infrastructure and their embodied environmental impacts are the next biggest contributors in the environmental footprint of the formed MWCNTs. Notable impacts are seen for the human toxicity, freshwater eutrophication and the ecotoxicity of freshwater and marine environmental receptors.

The individual contributors to the infrastructure environmental footprint is shown in Figure 4-8, detailing the furnace componentry parts. The impacts of the mass flow controller and mechanical syringe pump infrastructure portray a similar breakdown, and illustrate the intrinsic impacts associated with the extraction and processing of ores, precious metals and other highly refined materials that go into the construction of the devices. There are no examples in the literature for the impacts of the equipment involved in MWCNT synthesis being reported, the ability to measure this in the context of the overall environmental footprint provides an insight into the importance of more detailed LCA studies; such as in this chapter.

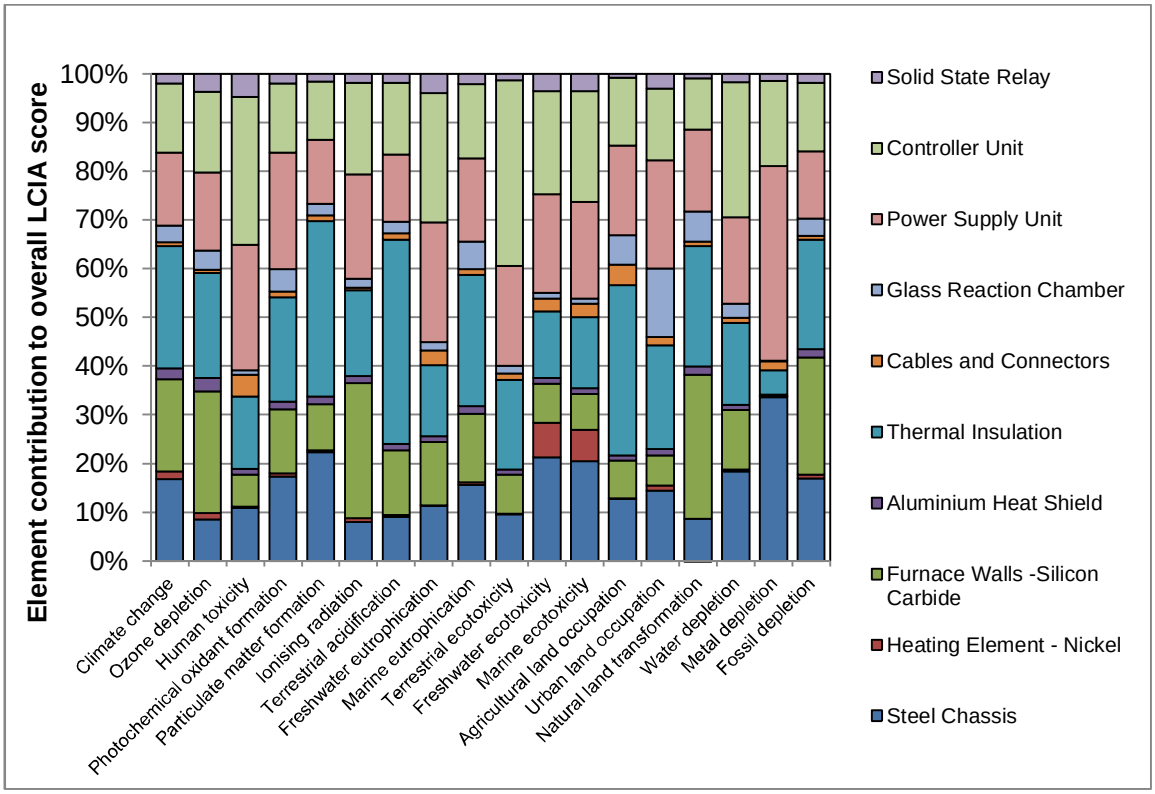


Figure 4-8 Percentage breakdown of the characterised impact contribution of different elemental parts of the furnace used for MWCNT growth.

4.4.6 *CHEMICAL PRECURSOR IMPACTS*

Argon use during the MWCNT growth phase shows an imprint across many categories, highlighting that efforts in the recycling of the inert carrier gas would be a beneficial avenue to explore in future process enhancements. However, in the context of this study the impacts due to chemical feedstocks, catalyst materials, hydrogen gas and hydrochloric acid use have a minor impact on the overall footprint of the formed MWCNTs.

The inclusion of ferrocene usage in the LCA, deemed missing from other studies (Upadhyayula *et al.* 2012), shows it is of little importance in the context of the whole system impacts. However, covering this missing input (APPENDIX D:), from the assessment of ferrocene production patents (Cordes 1965), and other literature associated with ferrocene production (Oxford 1996; National Center for Biotechnology Information 2011a) has allowed focus to be shifted onto what are the important parameters in the formation of this nanomaterial. The detailed LCI dataset of ferrocene will be of use also to those in wider LCA fields of research.

4.4.7 *SYSTEM EXPANSION: END-OF-LIFE TREATMENT*

Once the MWCNTs reach the end of their serviceable lifetime it is very likely that the material will be disposed of rather than recycled. Since at present no recycling or re-use of CNT materials occurs. Much debate surrounds the likely end-of-life treatment of CNTs (Renn and Roco 2006; Wardak *et al.* 2008; Bystrzejewska-Piotrowska *et al.* 2009). Arguably, incineration is a frontrunner (Holder *et al.* 2013). since the combustion of nanotubes occurs in the presence of air/oxygen at elevated temperatures of 695 °C (Pang *et al.* 1993). A recent investigation (Todea *et al.* 2013) using near identical laboratory equipment to those assessed in this system found no nano-particulate exhaust emissions for polymer-based plastics, both containing and not, CNTs.

The 695 °C incineration temperature is under the legislative requirement set by industrial emissions directive (European Commission 2010), where a temperatures of 850 °C for normal waste, and 1100 °C for hazardous waste must be met. Therefore any hazards from MWCNT containing products will very probably be mitigated through normal waste treatment channels.

Although outside of the cradle-to-gate boundary, since it 'skips' an in-use phase, the end-of-life disposal of MWCNTs has been estimated and shown in Figure 4-7. In order to benchmark the end-of-life contributions, a 'worse case' is modelled, representing a half hour burn-off period utilising the furnace operating at the same temperature as during reaction 790 °C. This is considered an upper bound account, since it is very likely that the furnace could take multiple batches of CNTs when the purpose is incineration as opposed to prescribed and characterised MWCNT growth.

There are iron nanoparticles present on the surface of the formed MWCNTs. The task of acid purification is present to remove the iron when a pure sample of nanotubes is required. However, if the goal was to retrieve the metal for an environmentally beneficial purpose then this is not a route worth pursuing, as shown in Figure 4-9. These impacts were calculated for a one hour sonication of the MWCNTs in the presence of hydrochloric acid.

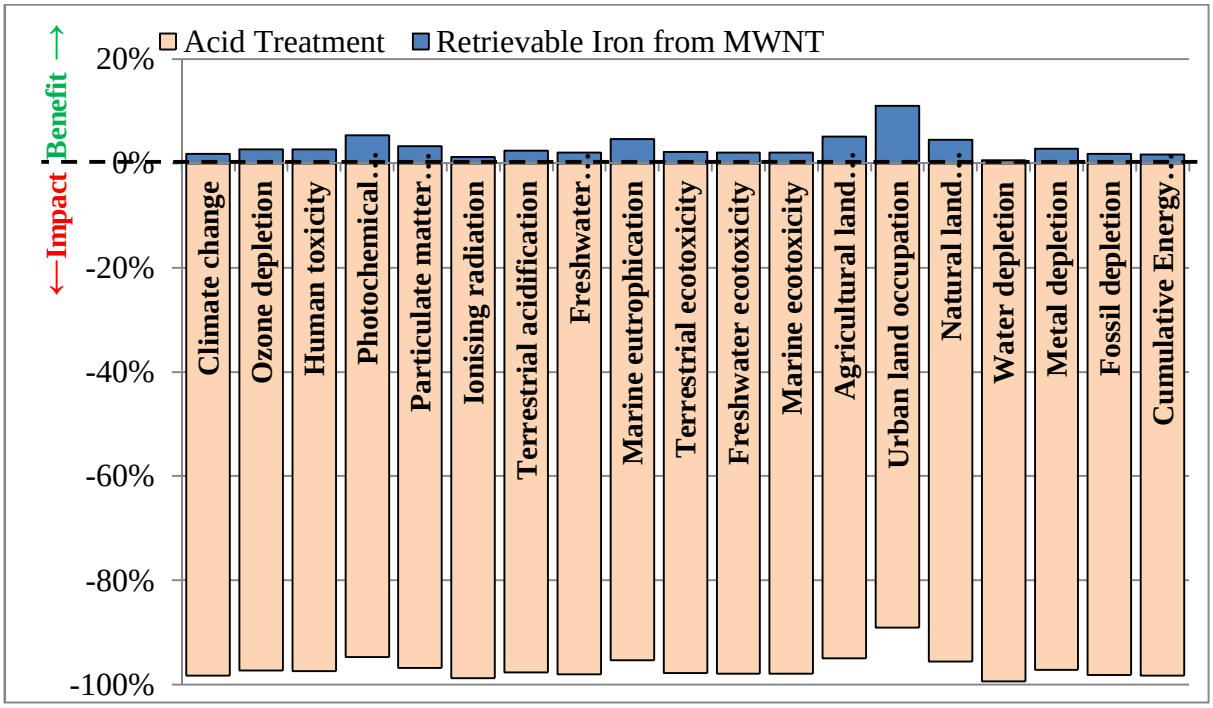


Figure 4-9 Potential impacts of a metal retrieval step via acid dissolution and sonication.

4.4.8 *RESULTS OF CUMULATIVE ENERGY DEMAND*

Energy usage has been identified as a major impact in the synthesis of MWCNTs this is in-line with others who have reported on the synthesis of ENMs. Further to the direct

and measurable use of energy during the synthesis of MWCNTs, embodied energy is present in all process input chemicals, infrastructure components, gases etc.

Figure 2-7 helps to clarify where energy consumption is occurring in MWCNT synthesis. The direct process energy consumption is indeed the largest contributor, with a total share of 85% of the overall process energy demand. Upon closer inspection 57.7% of the energy is required to heat the furnace from ambient to reaction temperature, 24.4% is necessary for the reactor during the MWCNT growth phase and 2.8% for the ancillary mass flow and feedstock supply equipment. Chemical impacts represent 13% of the energy consumption, with a mere 2% attributable to the reaction infrastructure equipment embodied energy.

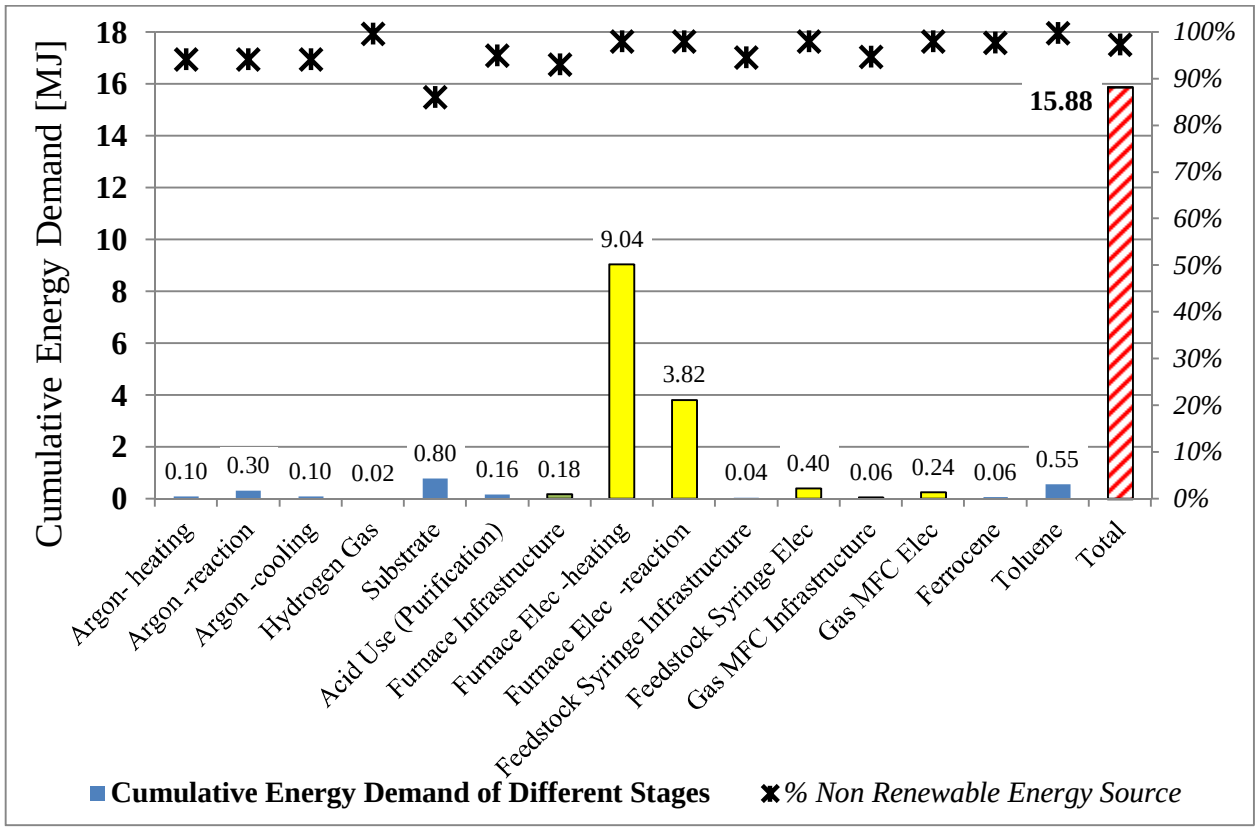


Figure 4-10 Cumulative energy demand of the different stages of MWCNT synthesis.

The ferrocene and particularly toluene usage have relatively high CED values in the context of the studied system. This is due to the higher heating value, or calorific content, of these combustible chemicals and of the pre-cursor chemicals involved in their synthesis. The origin of the toluene dataset lies in published literature of Plastics Europe (2011), they quotes the use of this 'feedstock energy' as being in addition to the

traditional input-output approach of LCA methodology, and represents hydrocarbons that have been 'diverted' from use as potential fossil fuel energy carriers; hence the need to account for this resource use.

Quoting energy usage alone is not instructive in accounting for environmental burden of a particular system, but rather the: source, method of extraction, delivery and associated emissions of this energy that carries the incumbent environmental impacts. The CED method in addition to absolute consumption provides insight into the nature of the source of energy use, the secondary axis of Figure 4-10, shows percentage of non-renewable energy used. Non-renewable energy use across the system lies between 86.1% and 99.8% of the total energy consumption at each input.

4.4.9 *RESULTS IN CONTEXT OF OTHER RESEARCH FINDINGS IN THE FIELD*

Using the cradle-to-production gate system boundary, as shown in Figure 4-3, the life cycle CED for the formed 300 mg of MWCNT product is 15.88 MJ; this translates to a MWCNT product with a specific energy 52.9 GJ/kg. If the furnace heating period were to be negated for a moment, then the embodied energy of growing the MWCNT would be approximately 22 GJ/kg (6.6 MJ/batch). Therefore, with reference to Figure 4-11 this process can be considered energy efficient in the context of similar reported materials made, especially when the enhanced efficiency measures are adopted.

When compared to conventional bulk materials such as: virgin steel ~35.3 MJ/kg, general plastics ~80.5MJ/kg, and virgin aluminium ~218 MJ/kg (Hammond and Jones 2008b; Hammond and Jones 2008a); CNTs can be appreciated as materials which are orders of magnitude more energy intensive. However, these industries have been perfected over many decades, and as discussed in Chapter 2, ENMs are typically used in much smaller mass quantities than traditional material counterparts to achieve similar functional abilities.

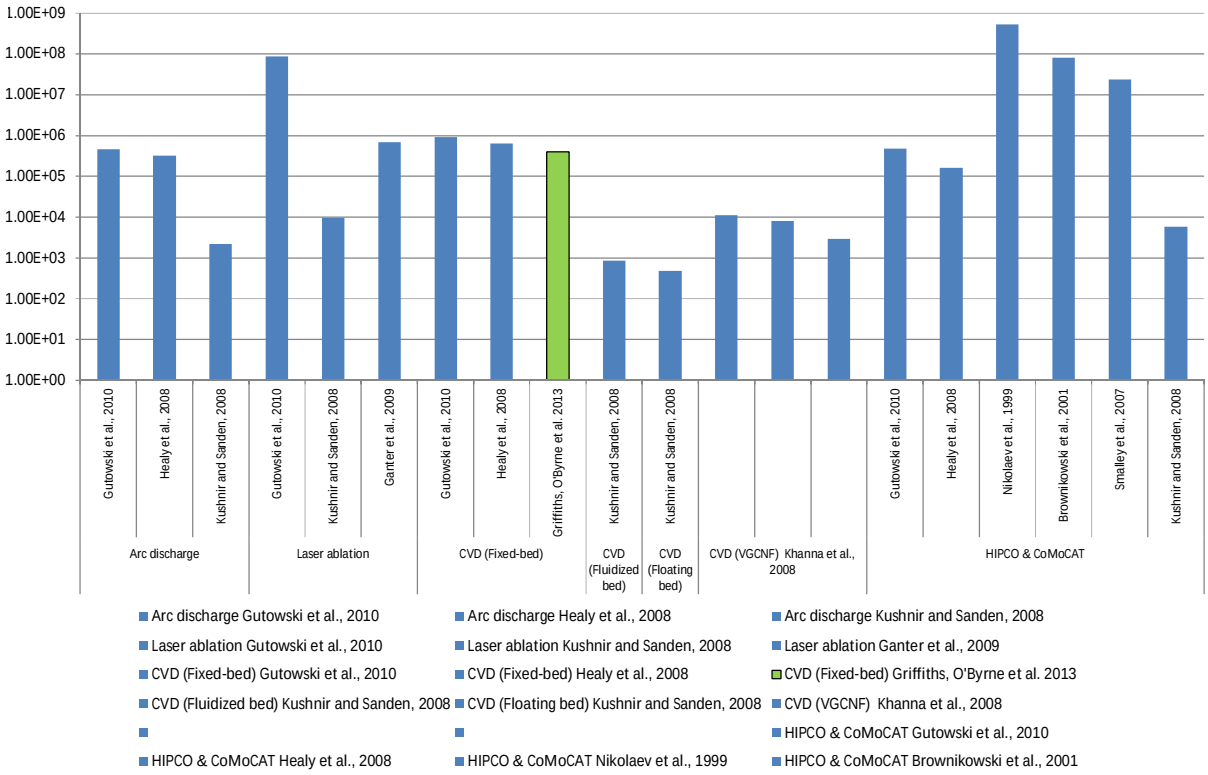


Figure 4-11 Energy Intensity of CNT product, MJ/kg. The CVD MWCNT process, coloured green, in comparison to other reported carbon nanotube / nanofibre energy densities.

Data plotted from values collated from (Upadhyayula et al. 2012). References for the different studies present beneath horizontal axis.

4.4.9.1 Nano-specific LCIA Findings

In section 2.1 of this chapter the LCIA results for all covered life cycle elements are shown. However, missing from this are impacts from the potential release of MWCNT product into the environment. CNTs have demonstrated toxic responses in various studies, but no widespread consensus has yet to be established with regard to environmental and human health impacts that might directly result in releases of this material class.

Eckelman *et al.* (2012) can be considered as a first attempt to try and unify and relate CNT production impacts versus the potential environmental impacts that would result from their release into the environment. This was achieved using the USEtox model (Rosenbaum *et al.* 2008).

USEtox is an emerging model, which attempts to provide a wider capture and harmonisation of chemicals presently covered in existing LCIA methodologies. Intended to formulate characterisation factors concerning chemical releases to the environment, the model is presently concerned with two environmental indicators: ecotoxicity effects via damage to the aquatic ecosystem, and damage to human health. USEtox is different to most other impact assessment methodologies, mostly since…

> *"…USEtox does not make use of a reference substance, but expresses the characterization factors in terms of comparative toxic units (CTU) per kg emitted. […]*
>
> *The characterization factor for aquatic ecotoxicity impacts (ecotoxicity potential) is expressed in comparative toxic units (CTUe), an estimate of the potentially affected fraction of species (PAF) integrated over time and volume, per unit mass of a chemical emitted.*
>
> *Unit: [CTUe per kg emitted] = [PAF × m³ × day per kg emitted]" (Rosenbaum et al. 2008)*

Although subject to uncertainties and limited in scope, the methodology is founded on a few current toxicology, fate and exposure literature reports. Following the USEtox framework, Eckelman et al. produced characterised impacts for worst and best case scenarios. Both cases shared the commonality of CNT effect on aquatic organisms, however, the differences between reported CNT fate and exposure in the environment is responsible for the discrepancy between the two; for instance, the longest reported CNT prevalence in the environment is reported to be months in the worst case, whereas the 'realistic' case considers the settling of CNT out of suspension to be days.

If the 0.3 g assessed in this chapter were to be released, the resultant impacts would be:

- 8.7 CTUe in the worst case, and
- 1.1 CTUe for a 'realistic' case.

These values are to be considered in the context of a life cycle in which the CNTs are to be included within. The USEtox LCIA model was applied for the life cycle activities

involved in the batch synthesis of the MWCNTs assessed in this chapter. The Simapro LCA software contains the USEtox model (Rosenbaum *et al.* 2008).

In terms of the cradle-to-gate impacts of forming the 0.3g batch of MWCNTs the impacts vary from between 94.91% to 0.24%; indicative of the uncertainty and disparity due to the relatively few existing studies in which the model is based upon. The 0.1% release values is considered a realistic case for fixed CNTs, as reported in chapter 2, the release of fixed ENMs during the life cycle is expected to be minimal (Gottschalk and Nowack 2011).

Table 4-7 Comparing the impact of MWCNT release versus MWCNT production, using the USEtox aquatic ecotoxicity measure. Units, comparative toxic units (CTUe)

Batch environmental release of MWCNT,				**Batch production of MWCNT**	**Release as overall cradle-to-gate %**
Modelled Scenario	**CTUe/kg †**	**Release (kg)**	**Resultant CTUe**	**USEtox - interim**	
worst	2.90E+04	3.0E-04	**8.70E+00**	**4.67E-01**	**94.91%**
best	3.70E+03	3.0E-04	**1.11E+00**	**4.67E-01**	**70.40%**
best -0.1% release	3.70E+03	3.0E-04	**1.11E-03**	**4.67E-01**	**0.24%**

In the context of a fuller life cycle Hischier (2013) applied the same values in his PhD thesis, and found the impacts of CNT release to the environment to be negligible, ~0.003%,. even considering the worst case characterisation factors developed by Eckleman et al. However, this value was taken as part of the whole life cycle of a 37" television set, in which the CNTs were but a part of.

In summary, with regard to CNT release specific impacts, the part CNTs play in the overall life cycle impact results of Hischier (2013) study can be deduced as followed:

- Production phase is ~ 80% of overall life cycle (use is ~20 %)
- The panel in which CNTs are incorporated equates to ~ 8% of production

- CNTs themselves are untraceable impacts in the context of this panel. Maximum of 1%.

- Thus for Hischier's case study, 'CNT production: CNT release' in context of whole life cycle is approximately 0.064% : 0.003%.

Appreciably, the impact of gate production versus CNT release is not a valid measure and requires consideration in a wider life cycle context. However, it is likely to be minimal in the context of the overall life cycle of the CNT life cycle, more validation and follow on studies is required (Eckelman *et al.* 2012).

Limitations of the model are recognised within Eckelman *et al.* (2012). These include relation to the CNTs being released, which can vary in their lengths, diameters, purity, form, agglomerate nature etc. These physical factors will change the environmental behaviour of the material, toxicity and fate. Therefore, although these results provide and indicative first estimation of impacts, future work will need to be more tailored towards specific CNTs rather than the class as a whole.

4.5 SENSITIVITY ANALYSIS: *'LEAN'* PROCESS AND THE POTENTIAL FOR LOWER IMPACT MWCNTS

The LCIA results of section 2 of this chapter have identified where the environmental hot-spots, a.k.a. high impact life cycle activities, exist for MWCNT synthesis *via* CVD. The identification of discrete contributors allows the possibility to propose solutions to minimise these is a very valuable outcome of the work. Previously in section 4.4.9 the batch formed MWCNTs were shown to be favourable in comparison to other similar CNT products. There are addressable parameters, however, for significant reductions in the environmental footprint of the MWCNTs to be achieved. This section presents implementable changes and adaptations for the environmental improvement of the system.

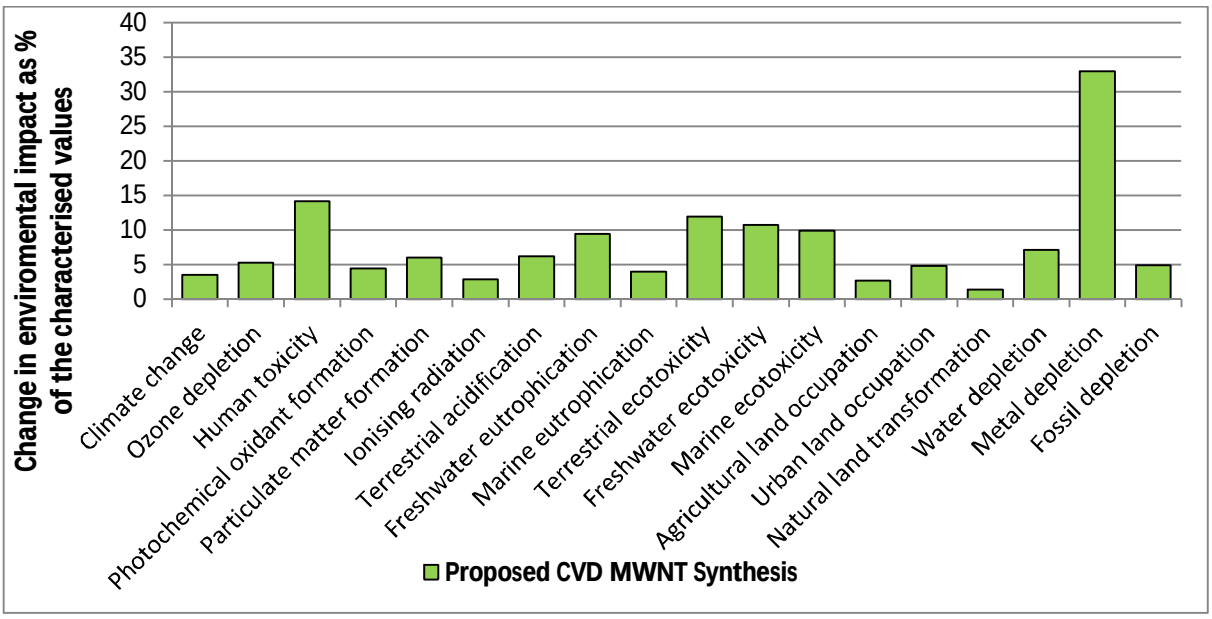


Figure 4-12 Impacts of proposed 'lean' MWCNT synthesis in comparison to the existing laboratory setup.

4.5.1 *REDUCED ENERGY USAGE DURING FURNACE RAMP-UP*

It was shown in that the furnace heating period, 'ramp-up', during which the furnace is heated from 0 - 790 °C, consumes over twice as much energy as that used during the growth period of the MWCNTs, see Table 4-2 and associated impacts reported in section 4.4.3. However, it is highly unlikely that any form of larger-scale production would have to heat the reaction chamber from ambient conditions for each synthesis. As the process moves more towards a continuous process, it is likely that the reaction chamber will be kept at a more constant elevated temperature between batches.

As an assumption the allocation of energy required in the heating period is distributed amongst five batches of MWCNTs. The non-flow properties of carbon nanotubes means, unlike traditional chemical engineering process (Agboola *et al.* 2007; Singh *et al.* 2008), that physical removal of the deposition site is required to retrieve the grown MWCNTs. Cooling, or at least a period of furnace operation without growth will be present and thus this assumption is a starting point for addressing impact reduction and process efficiency with increased scale quantities of MWCNTs. In terms of the GHG savings these changes result in impacts approximately 3% of the reference case assessed, with the vast majority of this improvement down to synthesis energy impacts, shown in Figure 4-13. The ancillary mass flow meter equipment has a lesser witnessed

improvement since although furnace usage is curtailed, there is still the same requirement for feedstock injection during the reaction, and a gas flow to be monitored, albeit for smaller flow quantities across the majority of the synthesis process.

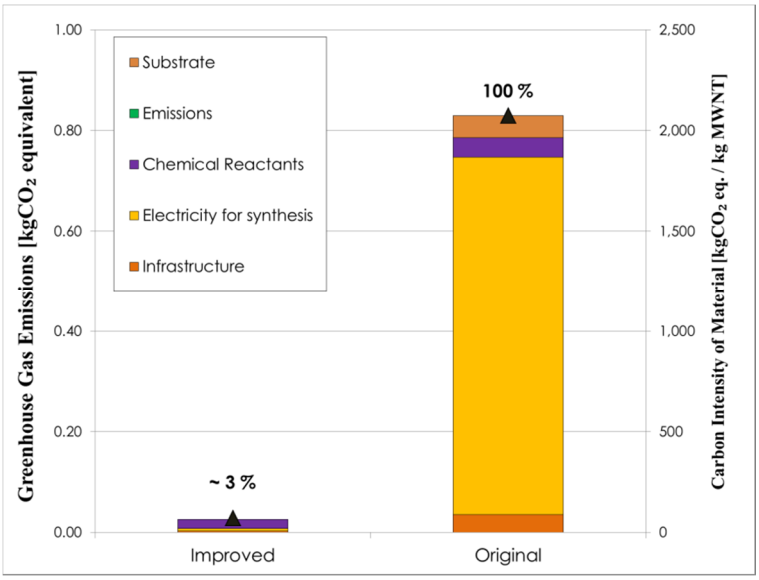


Figure 4-13 Carbon saving potential from proposed changes in this section

4.5.2 *CHANGING ELECTRICITY SOURCE: RENEWABLE EXPLOITATION*

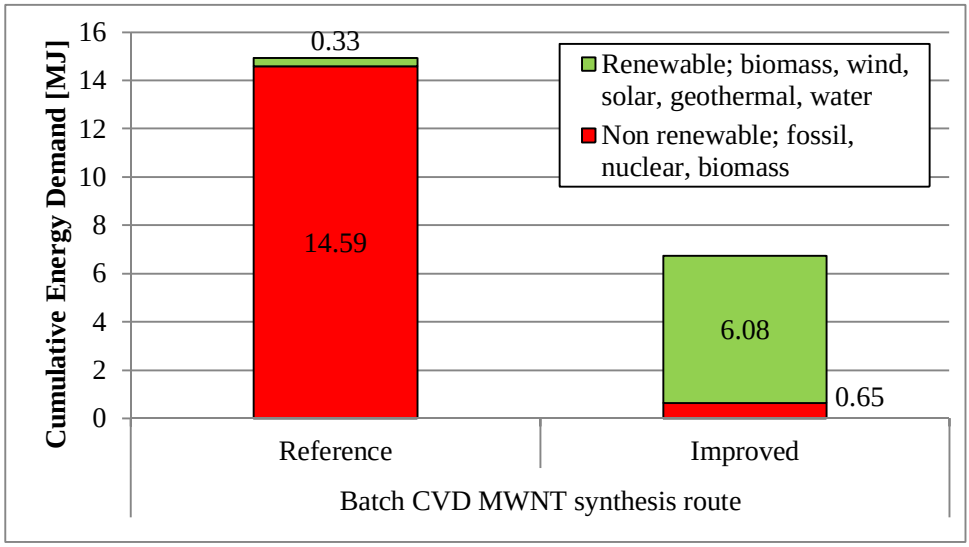


Figure 4-14 Two-fold gains in quantity and nature of the energy consumed in producing 300 mg of MWCNT product.

Adopting lean laboratory practices, predominantly thermal ramp-up periods, has the effect of reducing the specific energy usage for growing a batch of formed MWCNT to less than half with reduced ramp-up time, shown in Figure 4-14. The use of renewables electricity also accounts for a significantly increased total of the consumed energy, increasing from 2% in the reference case to 90% in the optimised and improved scenario.

4.5.3 *REDUCED INFRASTRUCTURE DEPENDENCY*

Two significant changes were made for the modelled impact/dependency of the infrastructure usage. Firstly, in moving towards a more continual 'lean' rather than batch-like synthesis process, the lesser heating period, for each batch of MWCNTs has the effect of reducing the infrastructure embodied impacts onto the formed product, since the MWCNTs spend less time inside the equipment. Secondly, instead of 2 batches per day being taken as a reasonable operator-led process flow, the proposed modelled dataset looks at the hour usage of the equipment as a proportion of its total lifetime, i.e. the pieces of infrastructure are constantly being used as if part of a continual industrial-like system.

4.5.4 *INPUT FEEDSTOCK RECYCLING*

Moreover, further gains in chemical impacts are achievable when considering the composition of the exhaust gas emissions, where a significant amount of toluene and its derivatives are present. As reported by others (Plata *et al.* 2009), the re-use of unreacted products in the exhaust indicate the potential for improvement in terms of reduced injection of toluene in the first instance, or if process mechanisms require this concentration at the reaction site then the emitted content of toluene could be recycled for further MWCNT synthesis. Without definitive values other than the exhaust emission measurements an assumption has been taken that half of the toluene could be recycled for subsequent MWCNT batches.

Ferrocene re-use has not been explored in this investigation, it is expected that all iron will remain deposited and will not be emitted into the exhaust streams. The quantity of ferrocene, only 0.2g rather than the 10ml of toluene, is a smaller overall process input meaning that recovery and separation from other exhaust species would be significantly more involved than toluene re-use. Iron, present and deposited by the ferrocene, has been found to be an almost negligible impact in the context of this LCA, therefore further end-of-life treatment/recovery, and the impacts these would incur, might be considered an inherently unfeasible option to pursue.

4.5.5 *OTHER CHANGES*

The impact of chemical usage is minimal in the context of overall process impacts, however, with lessening impacts of the dominant energy usage the smaller impacts become proportionally more significant. Argon usage proportionally drops with reduced furnace heating times, a further assumption was taken that Ar usage is completely stopped during the MWCNT cooling phase, proposing that the reaction chamber can be sealed and left to cool under a static rather than flowing presence of inert gas.

The consumption of hydrogen was found to be almost immeasurable in the context of the assessed system. The use of a renewable hydrogen datasets, see chapter 3, has been employed however within the suite of proposed potential improvements to the system.

4.6 MWCNT PREPARATION FOR CATALYSIS APPLICATION

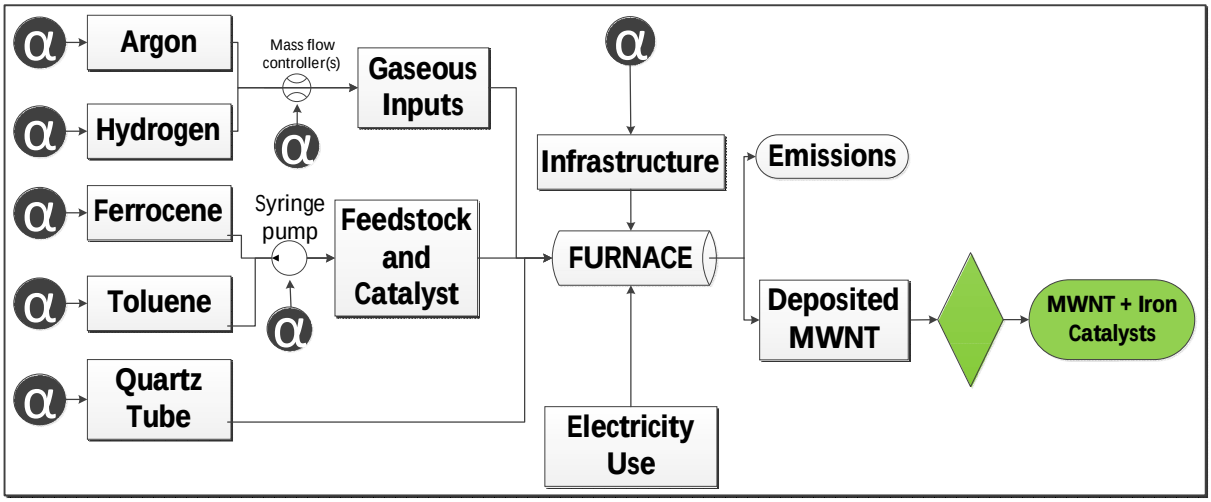


Figure 4-15 Life cycle stages covered in this section, the diamond represents the choice of post-MWCNT growth options for catalyst preparation.

Up to this point in the chapter, the scope of the LCA has been for a purified MWCNT product. In this section this boundary is expanded upon to cover further stages of preparing the MWCNTs for use as catalysts. The active catalyst material common for both catalysts is iron, the differences between the two post-treatment lies in how the iron is introduced, this choice of MWCNT post treatment for the addition of iron, is represented as the green diamond of Figure 4-15.

The green diamond is essentially representing either an iron activated (Fe@CNT) process, or an iron decorated (Fe_dec_CNT) process, the major stages of which are shown in Figure 4-16.

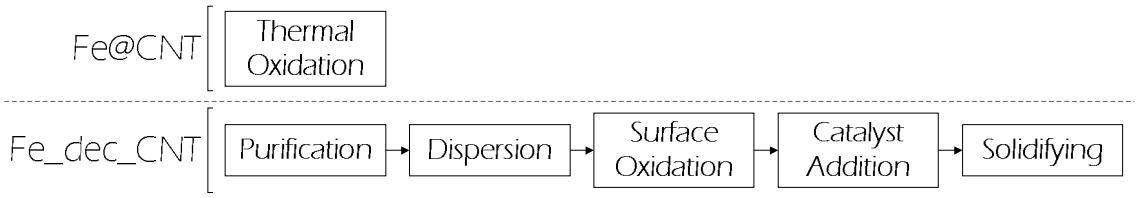


Figure 4-16 Two parallel processes for introducing nano-iron for MWCNT catalytic use

In the reference CVD MWCNT synthesis, elemental iron is required as an initiator for nanotube growth. Iron is also a key metal in the Fischer-Tropsch catalysis process (Dry 2002; Davis 2007), therefore the trace quantities present in the material have the potential to serve two catalysis processes: the initial MWCNT growth, and subsequent Fischer-Tropsch catalysis application. As previously stated post-synthesis MWCNTs have inherent impurities as a result of the deposition of catalytic debris such as carbon soot and trace amounts of elemental iron. Often, the impurities are removed *via* an acid treatment process, as covered in the previous section. The Fe@CNT route, however, does not consider iron as waste debris, but a dormant active ingredient on the MWCNT surface.

Collaborators in this LCA have published a novel method of MWCNT 'debris–iron' activation for Fischer-Tropsch catalysis (O'Byrne *et al.* 2013) effectively synthesising the substrate and active catalyst materials in a solitary synthesis step. The differences in Fe@CNT and Fe_dec_CNT synthesis, outlined in Figure 4-16, and perceived catalyst performance reported in the work (O'Byrne *et al.* 2013) warranted further investigation in terms of their life cycle performance to quantify the environmental benefits of the novel Fe@CNT route.

4.6.1 *REFERENCE 'FE_DEC_CNT' SYSTEM*

Traditionally in catalyst preparation steps, the MWCNT product is purified after its initial synthesis. Once purified a sequence of cleaning, and preparing the surfaces of the MWCNTs to receive nano-metals is undertaken, before finally mixing both ingredient to produce MWCNTs 'decorated' with the nano-iron catalyst material. The steps of forming the iron decorated MWCNT (a.k.a. Fe_dec_CNT) are covered in Figure 4-17, and all associated inventory data is presented in the associated APPENDIX C: of this chapter.

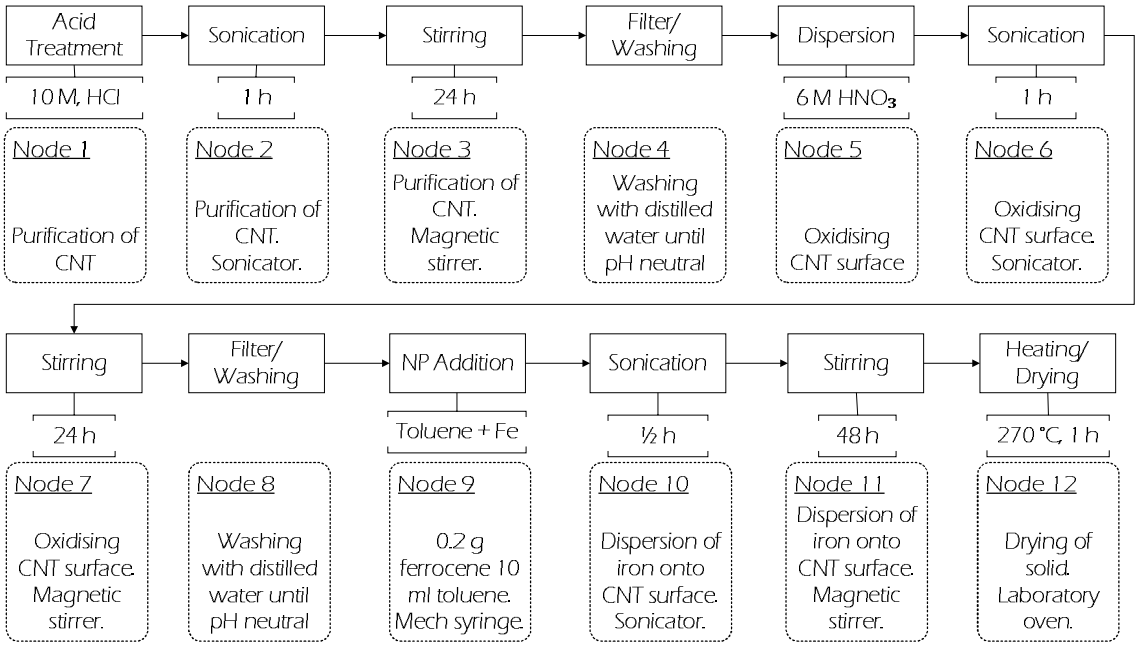


Figure 4-17 The twelve nodes for iron decorated carbon nanotubes; linking synthesis and catalytic use of nanotubes

4.6.2 *NOVEL 'FE@CNT' SYSTEM*

In the new proposed route, the process activates the embedded iron nanoparticles left over after MWCNT growth. The majority of the iron has a carbon/graphitic coating hindering contact between the metal and any potential reactant gases. Thus a 'burn-off', or thermal oxidation, of outer carbon layer is performed which under specified conditions does not breakdown the MWCNTs themselves and only targets the coated iron elements.

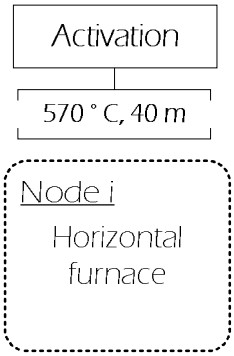


Figure 4-18: Single-step activation stage for iron @ carbon nanotubes; linking synthesis and catalytic use of nanotubes

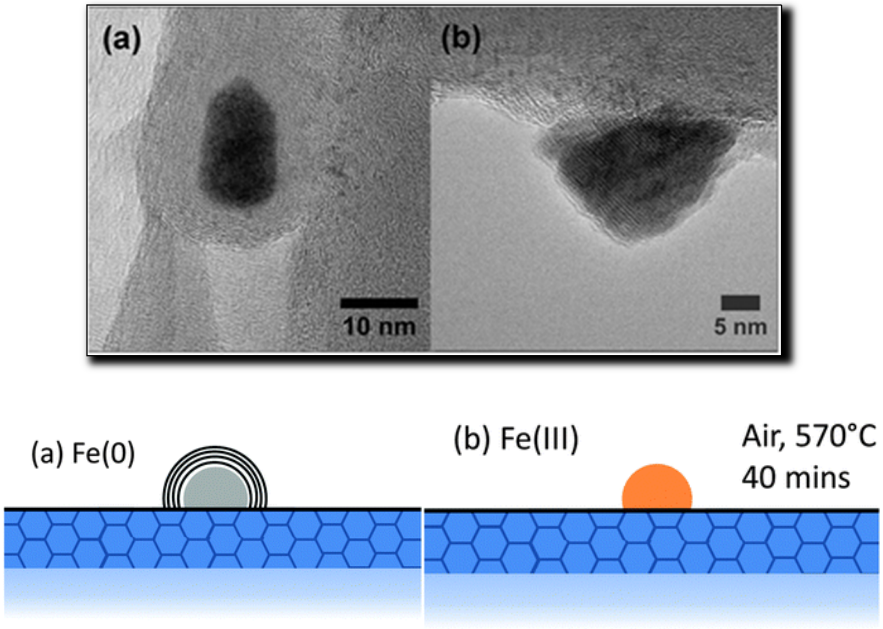


Figure 4-19: Electron microscopy and schematic diagram of the oxidation of formed MWCNT to produce Fe@CNT catalysts.

(a)Graphitic coated iron nanoparticles as they are immediately after MWCNT growth, (b) the iron nanoparticles once the carbon coating is burnt off, revealing iron nanoparticle. Image and graphics used with author permissions (O'Byrne *et al.* 2013)

4.6.3 *COMPARISON OF IRON ACTIVATED AND IRON DECORATED MWCNTS*

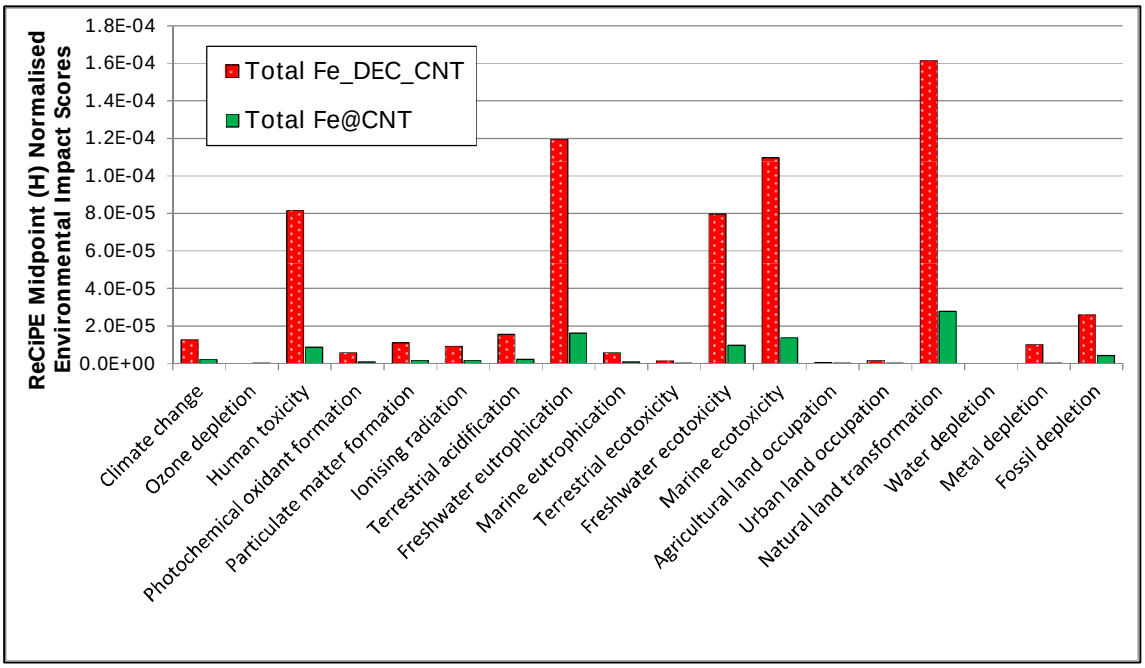


Figure 4-20: Comparison of the embodied impacts for the additional preparatory stages required to make the MWCNTs catalysts for CO_2 conversion. Either *via* decorated nanotube addition of iron nanoparticles, or activation of pre impregnated elemental iron nanoparticles.

Figure 4-20 displays the impact of the life cycle activities performed on the MWCNT product, to be added in addition to the impacts shown in Figure 4-7 (page 87). The impacts of Fe_dec_CNT preparation stages would be considerable amongst the prior MWCNT synthesis life cycle stages, placing it the second most impactful stage – above that of infrastructure and chemical usage. The Fe@CNT synthesis on the other hand has the immediate benefit of contribution to minor impacts across all categories and the negation of a purification stage; a compound benefit for adopting this alternative route.

4.7 MWCNT LCA CONCLUSIONS

Two predominant needs are fulfilled by the work contained in this chapter; of immediate context is the accurate account of a carbon capture utilisation process, employing MWCNT as a candidate material (Minett *et al.* 2013; O'Byrne *et al.* 2013) covered in chapter 6 of this thesis. Additionally, the contribution and impact of the LCA work provides transparent and detailed life cycle inventory data, which addresses missing gaps within the field (Upadhyayula *et al.* 2012).

The impact of energy usage in the CVD MWCNT growth process was found to be the dominant life cycle activity, this finding is in line with other studies in the field (Healy *et al.* 2008; Khanna and Bakshi 2009; Upadhyayula *et al.* 2012). The greater depth of assessment has shown infrastructure to be of a significant secondary contributor to the overall life cycle burdens, this is an aspect found missing from other studies. The impact of infrastructure might very well decrease with further process optimisation and industrialisation, although the synthesis of MWCNTs are for at least the foreseeable future, likely to be intensive (Agboola *et al.* 2007; Singh *et al.* 2008) and thus the formed MWCNTs will likely be more intensive than other fine chemical products.

Chemical constituents including the hydrogen gas, ferrocene catalyst and toluene carbon feedstocks have only trace impacts on the overall life cycle. The impact of ferrocene was identified as a missing element from LCAs to date, indeed the formation of this modelled dataset founded on an industrialised patent (Cordes 1965) and other supporting literature (Oxford 1996; National Center for Biotechnology Information 2011a), although proven to be of lesser concern in this study will be of use to those seeking to estimate the impacts of the material and other metallocenes; a widely used class of materials (Nesmeyanov and Kochetkova 1974; Amer *et al.* 2010; Werner 2012).

The carrier gas argon has a marked impact on MWCNT synthesis, this impact is the combination an intensively produced gas in conjunction with high volumes usage (necessary to protect the MWCNT from oxidation and provide a satisfactory carrier medium for chemical reactants) is unavoidable. However, if argon gas were to be recycled then this impact, could be shared across many multiple batch synthesis, greatly reducing the impact. The exhaust gas emissions were also assessed based on samples taken during the growth phase, if left untreated these would present dominant impacts in the production of photochemical oxidants.

Through a 'lean' scenario analysis the production of a lower-impact MWCNT product was investigated, founded on a combination of process changes: higher throughput of materials and the use of a lower impact wind power provision and electrochemical hydrogen gas production. Together with gas recycling of unreacted chemical reactants, as proposed by others investigating CVD synthesis emission products (Plata *et al.* 2009), and argon carrier gases. These changes would have an impact-category wide effect of

reducing MWCNT impact to 10% of the current process. Since impacts of process are in alignment with others investigating MWCNT synthesis, for reported cumulative energy demand at least (Healy *et al.* 2008; Upadhyayula *et al.* 2012), then the opportunity for reduced impacts warrant further investigation. In the context of full LCA an in-depth usage phase would require evaluation to establish the full extent in which these materials perform compared to materials they might displace for given applications.

An end-of-life, incineration phase was modelled for the MWCNT products, this benchmark was based on other work in the field (Holder *et al.* 2013; Todea *et al.* 2013). Incineration is found to be the second-largest life cycle impact after the energy required in the initial MWCNT growth.

Two routes of preparing MWCNTs for use as catalysts in the conversion of CO_2 to hydrocarbons were investigated, the second is novel amongst the field of MWCNT (O'Byrne *et al.* 2013). A novel approach of activating the iron left over in the initial synthesis of the nanotubes is found to be far less impactful than a traditional route. This result indicates the benefit of being mindful of the final application of the engineered nanomaterial, tailoring the process to reduce unnecessary processing and purification stages.

Additional contributions of this work include the characterisation of the MWCNT product used, important when impact assessment methodologies and risk assessments expand to quantify the potential impacts of these in the environment. When MWCNTs are used as catalysts, and indeed in other fixed applications, the release of free nanotubes into the environment is very unlikely, however, it may be of concern for other applications where wear and degradation are potential release pathways.

Through the use of a MWCNT release model produced by Eckelman *et al.* (2012) and founded on USETOX (Rosenbaum *et al.* 2008). The unhindered release of the MWCNTS has the potential to cause more aquatic ecotoxicity impact than the life cycle synthesis activities; however, this is a preliminary assessment model. Additionally in the in situ- and fixed catalyst use, the likelihood of release is extremely unlikely.

Chapter 5: LCA OF NANO IRON AND PALLADIUM CATALYST SYNTHESIS

Highlights

- This chapter details the deposition of iron and iron-palladium nanoparticles onto mesoporous silica substrates, pore sizes ~ 6 nm. These materials were assessed as they have proven abilities as RWGS-FT catalysts, see chapter 6.
- Cradle-to-gate LCAs of 8 catalysts was performed in order to establish the environmental impacts inherent in their formation.
- The active catalyst metals were deposited in different amounts for the 8 catalysts; percentage weight loadings, relative to silica substrate mass, vary between 10 – 40 wt.% for iron content, and 0-4 wt.% of palladium content.
- Impact assessments results show electricity consumption and palladium content to be the most impactful life cycle activities, iron content and all other associated life cycle activities; infrastructure (apart from noted exceptions) and use of chemicals show negligible contributions in comparison.
- If GHG impacts were considered independently, then electricity usage would be highly dominant, but this ignores a vast quantity of other impacts, where palladium metal usage play significant to major influence.
- The use of palladium when it is introduced at even 1 wt.% loadings was found to be most dominant in the context of the whole gate synthesis impacts, across a large proportion of impact assessment categories. Enhanced global palladium recycling rates, and an end-of-life recovery of catalyst metals, could substantially lower the overall impact, but not displace palladium as the dominant impact.

5.1 INTRODUCTION: CHAPTER CONTRIBUTION TO THESIS AND WIDER WORK

This chapter provides a measure of the inherent life cycle environmental impacts of depositing iron and iron-palladium nanoparticles onto porous silica substrates *via* a technique of wet impregnation. The material application are catalysts for the reverse water-gas shift and Fischer Tropsch (RWGS-FT), converting CO_2 into hydrocarbons; this catalytic process and its specific operation is covered in chapter 6. Life cycle assessment (LCA) quantifies the cradle-to-gate impacts of forming the catalysts, a necessary first step in appreciating the environmental impacts of the whole process (Griffiths *et al.* 2013b).

There are limited studies conducted for the application of catalyst nano materials, but Lloyd *et al.* (2005) hypothesise a potential in-use benefit that would result from reduced platinum-group metals in automotive catalysts. Lavery *et al.* (2013) conducted a comparative assessment of two new methods of sponge nickel (micro rather than nano) catalyst formation and use, their findings show increased production impact, but improved in-use impact for the two impact categories of energy and carbon footprint measured. No LCAs pertaining to the production of nano catalysts could be found in the literature, therefore this work is contributing to this field where metal nanoparticle deposition as catalysts, an increasingly exploited technique (Astruc 2008). This work is therefore not only a stepping stone for establishing the complete life cycle performance of the RWGS-FT process, but also as a valuable intermediary for others seeking to measure the effects of nanometal and subsequent catalyst exploitation.

The synthesis route covered in this LCA is at a laboratory scale, differences would be expected between laboratory and industrial-scale material synthesis. However, the separating of intrinsic life cycle stages provides an appreciation of what impacts are likely to be present for all scales, and those in which could be addressed via process change. The transparent nature of this LCA work has a co-benefit of bridging LCA work between novel and established processes, another research area where much uncertainty presently exists (Hetherington *et al.* 2013).

5.2 CHAPTER AIMS

Objective 1. Establish the environmental impacts of forming the nanomaterials

Objective 4. Communicate to technology developers key life cycle results for action

Objective 5. Communicate wider environmental impacts

5.3 SCOPE AND SYSTEM BOUNDARY

The synthesis procedure detailed in this chapter is for eight catalysts, each with different loadings of iron and palladium in relation to the weight of silica substrate used. The goal is to establish the relative impact of forming the catalysts. Determining whether material content, or inherent processing steps are informative aspects when attempting to assess and improve upon the development of these materials for future application.

The system boundary of this LCA includes all laboratory processes and equipment involved in the synthesis of the catalysts, via the iron/palladium metal nanoparticle being deposited onto a mesoporous silica substrate. The process follows a succession of common stages:

1. Constant agitation and stirring to keep the amorphous silica particles suspended in methanol.

2. Addition of iron nitrate and, when applicable, palladium acetate solutions to the silica suspension.

3. Successive stirring and sonication steps (high frequency oscillation of solution) disperse and ensure thorough mixing of all solutes.

4. Evaporation of methanol solvent *via* a rotational evaporator, obtained product after this is a uniformly distributed fine powder.

5. Methanol evaporate from the previous step is condensed using a water jacket, and stored for subsequent repeat synthesis steps without requiring additional purification steps.

6. The dried silica – metal nanoparticle powder is heated at elevated temperatures of 500 °C, the result is a 'calcined' metal oxides.

7. In-situ within the reactor, hydrogenation of the dried catalyst with the metal nanoparticles activated to a reduced form ready for their application in catalysis.

The different stages are all elements within the system boundary, assessed independently for their contribution to the overall environmental impact of the obtained catalyst material. Figure 5-1 demonstrates the relationship between these stages, displaying the material flows and energy usage at the different points. [Note, after evaporator step there can be 4 batches fed into the furnace, due to capacity differences].

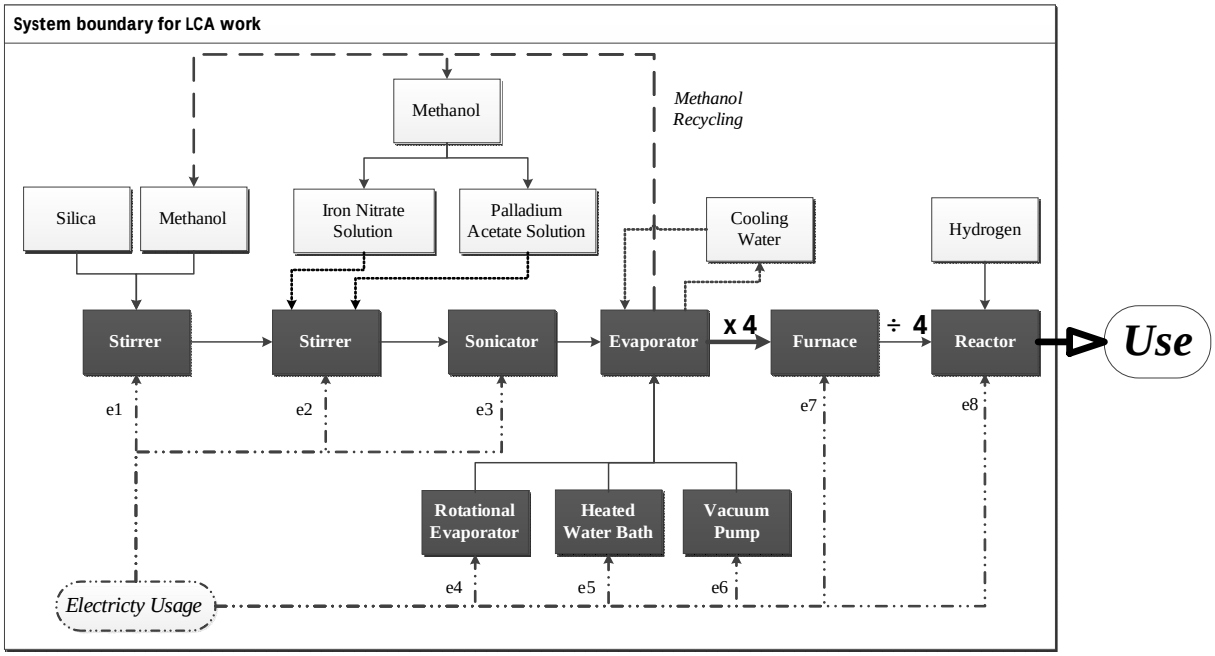


Figure 5-1 Process flow and system boundary of the wet impregnation technique of nano-iron/palladium onto amorphous silica. Flows annotated 'e' represent electricity consumption.

5.3.1 *FUNCTIONAL UNIT*

- The impacts of processes within the system boundary are related to 1.0 gram of catalyst material formed, i.e. the quantity used in its intended catalytic use stage. This 1.0 gram mass functional unit is not the same as a 'batch' of synthesised catalyst, as outlined in the system boundary of Figure 5-1. The batch weight

varies between 2.35 to 3.98 g dependent on the catalytic loading of iron and palladium respectively, see

.

5.4 INVENTORY DATA

The data used in this LCA study represents the best available at the time of conducting the analysis. Direct measurable process flows are recorded with a high degree of certainty, proxy datasets are used for the accounting of material and processing life cycle stages prior to those entering the assessed system boundary. Major inventory datasets include those covering, the:

- Material/chemical constituents: methanol, silica, iron nitrate, and palladium acetate.
- Laboratory Equipment: stirrer, sonicator, rotary evaporator, vacuum pump, heated water bath, high temperature furnace.

Table 5-1 Catalyst nomenclature, chemical composition, and resultant masses.

Name	Composition	$Fe(NO)_3.9H2O$	$Pd(OAc)_2$	Catalyst mass
Fe20	**20wt%Fe/SiO2**	**3.618 g**	**-**	**2.72 g**
Fe10Pd1	**10wt%Fe/1wt%Pd/SiO_2**	**1.626 g**	**0.047 g**	**2.35 g**
Fe20Pd1*	**20wt%Fe/1wt%Pd/SiO_2**	**3.664 g**	**0.053 g**	**2.75 g**
Fe30Pd1	**30wt%Fe/1wt%Pd/SiO_2**	**6.292 g**	**0.061 g**	**3.28 g**
Fe40Pd1	**40wt%Fe/1wt%Pd/SiO_2**	**9.811 g**	**0.071 g**	**3.98 g**
Pd1Fe20*	**20wt%Fe/1wt%Pd/SiO_2**	**3.664 g**	**0.053 g**	**2.75 g**
Pd2Fe20	**20wt%Fe/2wt%Pd/SiO_2**	**3.711 g**	**0.108 g**	**2.79 g**
Pd3Fe20	**20wt%Fe/3wt%Pd/SiO_2**	**3.759 g**	**0.164 g**	**2.83 g**
Pd4Fe20	**20wt%Fe/4wt%Pd/SiO_2**	**3.808 g**	**0.222 g**	**2.87 g**

* Identical catalysts, different nomenclature used to show impacts of changing Fe and Pd loadings respectively.

Per batch synthesis, the mass of silica remains constant - at 2.00 g - for all of the different catalysts. Catalyst variations occur from differing weight percentages (wt. %) of metal loadings with respect to the silica mass. The iron/palladium loading is controlled by differing amounts of iron nitrate nonahydrate $Fe(NO)_3.9H_2O$ and palladium acetate $Pd(OAc)_2$ respectively, see Table 5-1.

Iron loadings of the final catalysts sit between 10 to 40 wt.%, and up to 4 wt. % of palladium is present; added as a promoter. Apart from metal loadings, the preparation of each catalyst preceded using the same incipient wetness impregnation technique given in the account of the system boundary section 5.3 and Figure 5-1. More specific process information is contained within APPENDIX E: of this chapter, and in the PhD thesis of Rhori Owen, 2013, University of Bath.

5.4.1 *MATERIAL AND CHEMICAL USAGE*

Life cycle inventory (LCI) data for five primary flows of chemical material were required in this LCA study. The data used for modelling the chemicals used are shown in Table 5-2. LCI datasets exists for the more common methanol and de-ionised water used in the process, these were sourced from Ecoinvent database (Ecoinvent Database v2.2 2010) and were checked and deemed suitable in terms of best representation of likely production pathway and of grade suitable for use in the assessed process. No representative life cycle inventories for the amorphous silica, SiO_2, $Fe(NO)_3.9H_2O$, $Pd(OAc)_2$, compounds were available. To address missing data, research into the most prominent industrial pathways, and mass-balances of reactants and co-products involved in their production are established,

The entirety of the embodied impacts of the catalyst constituent materials, i.e. silica, iron nitrate and palladium acetate are present in the catalyst product. Only a proportion of the impacts in forming the methanol and de-ionised water are imparted onto the formed catalyst, since both methanol and water can be mostly recovered, making the liquids available for subsequent synthesis, or other processes. Assessed laboratory practices did not re-use methanol, due in part to the relatively small quantities used at this scale and potential impurities picked up during synthesis steps, thus to reduce workload new solvent was used each time. At a larger scale where a closed-loop process producing a specific catalyst the recycling of methanol would become an adopted approach.

When conducting the LCA for the laboratory process no recycling of solvent or coolant is modelled. However, for the 'lean' improved synthesis case, the use of methanol is modelled as being 95% recycled / re-used within the process, that meaning only 5% virgin methanol, or 2.5 ml, is needed per synthesis of the specific catalyst being formed. The extra efforts in re-using methanol are deemed negligible in this process, since a recoverable stream of methanol is already produced as a result of the required separation of the catalyst solids from the solvent. Similarly the de-ionised water, used to cool the methanol evaporate is modelled to be 95 % recoverable. In both cases, the 95% re-use value is an estimation, verified through laboratory measurements, set to account for evaporate losses at this stage.

Table 5-2 The Quantities and Inventory Data used for Chemicals

Chemical	Quantity	Origin of LCI Data
Amorphous Silica	**2.00 g**	**Own modelled dataset**
Iron Nitrate	**1.626 - 3.808 g**	**Own modelled dataset - stoichiometry**
Palladium Acetate	**0.047 - 0.222 g**	**Own modelled dataset - stoichiometry**
Methanol	**50 ml (95% re-use)**	**Ecoinvent**
De-ionised Water	**2000 ml (95% re-use)**	**Ecoinvent**
Hydrogen	**0.495 g (300 ml)**	**Ecoinvent**

Hydrogen gas injection occurs to prepare the catalyst(s) prior to the FT-RWGS catalysis use, this occurs under elevated temperatures, and once the catalyst is situated within the final reaction chamber. It is thus a 'bridging' life cycle step between the formation and use of the catalyst.

5.4.2 *INVENTORIED ENERGY USE IN THE PROCESS*

Table 5-3 Energy consumed by different points of the catalyst(s) synthesis life cycle

Flow Notation	Description of energy requirement	Absolute Energy Consumed [kWh]	% of Total Energy Consumed
e1	**Dispersion of silica in methanol solvent *via* stirring**	**0.0017**	**0.06%**
e2	**Stirring silica and metal solution(s) within methanol**	**0.0006 (or 0.0012*)**	**0.02%**
e3	**Sonication of silica + metal compounds**	**0.130**	**4.9%**
e4	**Rotational evaporator**	**0.009**	**0.34%**
e5	**Heated water bath**	**0.135**	**5.1%**
e6	**Extraction of methanol solvent *via* vacuum pump**	**0.026**	**0.97%**
e7	**High temperature furnace calcining of nanoparticles**	**2.043****	**76.5%**
e8	**Reactor activation phase of new catalyst material**	**0.29*** ramp-up**	**10.9%**
		0.035 reaction	**1.3%**

* When palladium acetate solution is used

** Each furnace run consumes 8.17 kWh, however 4 batches are heated with each run ≈ 2.043 kWh/batch

*** Ramp-up stage, the energy required to bring the reactor and material to the activation temperature.

Energy, specifically electricity in this study, is consumed at multiple points throughout the process. Table 5-3 provides an account of consumption across the life cycle; the first column refers to the annotated flows identified within the system boundary of Figure 5-1.

The values quoted in Table 5-3 are for the mean absolute energy consumption, measured directly per batch of catalyst formed. The quotient of the absolute energy values with the respective catalyst masses, shown in the table relates the energy

consumed to the functional unit of 1.0 gram of formed product. Therefore, the percentage values can be considered to be constant irrespective of catalysts made.

The energy readings were measured directly for the synthesis equipment. The low power consumption of certain equipment with values < 0.01 kWh are immeasurable with the meters used, and thus the steady-state readings of current across the used period were taken and resultant power calculated. The typical consumption of these devices was verified with their technical manuals. Repeated synthesis runs found the energy readings to be practically constant. It was deemed that exhaustive efforts in obtaining the exact values for devices consuming less than 0.1 kWh, were not matters for urgent address given their trivial contribution to the overall process.

From Table 5-3 the use of the furnace is the overall dominant energy consumer, responsible for 76.5 % of the total energy used throughout the process, the subsequent reactor heating and use accounts for 12.2%. The remaining life cycle stages, e1 to e6 have negligible impacts when compared to the final furnace energy consumption, especially those related to the stirring activities within the process.

5.4.3 *PROCESS INFRASTRUCTURE IMPACTS*

Collecting LCI data for the respective embodied impacts of the various infrastructure equipment, involved the partial or full disassembly of componentry parts. A full bill of materials was generated and the quantity of raw material determined, by computing the formed parts list, constructed with the help of respective equipment manuals and manufacturer data. Further checks were made by comparing the environmental footprints for other electronic devices listed in the available inventory datasets (U.S. Life Cycle Inventory 2008; Ecoinvent Database v2.2 2010), from a qualitative perspective the modelled footprints were comparable to other devices.

The accuracy of the infrastructure data capture is high. This is demonstrated by conformation of the produced inventory data, for one of the more complex infrastructure components, and then a subsequent communication with an engineer for the firm confirmed the parts list, nature of materials and their masses. The initial dataset almost comprehensively matched this independent account; providing confidence in the data generated for other devices whereby no manufacturer supplied information was

obtainable, or representative datasets available. This is a common LCA hurdle, whereby an iterative sense-checking approach of the data collection is required to validate the LCA work.

Table 5-4 presents an account of the equipment used during the synthesis of the catalyst materials. For the majority of the infrastructure devices, if a direct dataset was not available then data for component parts, and in some cases their precursor part would be available for a representative model to be made. An example of this approach is for the sonicator device, by mass almost entirely stainless steel, however. The high frequency driving forces are delivered through a 'horn', essentially similar to an audio loudspeaker, consisting of a ferrous core and copper windings; this is modelled from ferrite and copper winding datasets.

Table 5-4 Equipment Used in this Study

Equipment	Use
Mechanical stirrer	**Keeping reactants in solvent**
Sonicator	**Dispersion of metal into pores of silica**
Rotary evaporator + heated water bath	**Heating solvent and drying product**
Vacuum pump	**Removal of evaporated solvent**
Furnace	**Calcining of powder to produce catalyst**
Reactor	**Activation of catalyst for use phase**

5.4.4 *ALLOCATION OF INFRASTRUCTURE IMPACTS TO FUNCTIONAL UNIT*

Table 5-5 captures the proportion of total environmental footprint for each piece of infrastructure equipment used to produce one gram of catalyst. The allocation of impacts is based on the maximum batches the respective pieces of equipment could perform within their serviceable lifetimes. The allocation is laboratory governed, i.e. how many times is the equipment used to perform the dedicated function, in terms of its overall serviceable lifetime. By means of understanding this allocation the mechanical stirrer, sonicator and vacuum pump which had a measure of 1.37×10^{-4} means that 0.0137% of the total life cycle impacts of creating these devices must be attributed to each batch of catalyst formed. The specific environmental footprint per gram of material

was then established by dividing this batch-based impact with the mass of the formed catalyst; masses shown in Table 5-1.

Table 5-5 Proportion of equipment embodied environmental impact imparted onto each gram of catalyst material formed

Equipment	Lifetime in years	Operations per day	Embodied impact per gram of formed catalyst*
Mechanical stirrer	**10**	**2**	$\frac{1.37\times10^{4}}{\partial}$
Sonicator bath	**10**	**2**	$\frac{1.37\times10^{4}}{\partial}$
Rotary evaporator & water bath	**15**	**2**	$\frac{9.13\times10^{5}}{\partial}$
Vacuum pump	**10**	**2**	$\frac{1.37\times10^{4}}{\partial}$
High temperature furnace	**15**	**2**	$\frac{2.28\times10^{5}}{\partial}$
Reactor	**25**	**2**	$\frac{5.48\times10^{5}}{\partial}$

***Where ∂ is equal to the final mass of the specific catalyst formed (see Table 5-1).**

5.5 NANO-SPECIFIC INVENTORY ACCOUNTS

Combinations of iron, palladium, and iron-palladium nanoparticles supported on silica are produced during the synthesis of catalysts detailed in this chapter. The exact metal particle sizes are not constant, but range from 5 nm to 10 nm upwards, dependent on the amount of particle agglomeration that has taken place and the propagation at the deposition site on the catalyst.

The metal nanoparticles form (out of solution) once the metal ions are deposited on the silica support, an incipient wetness methodology elements are liberated from their respective solutions. As shown in Figure 5-2, the furnace / calcining and hydrogenation step are both possible points where nanoparticulate releases may occur; as do any use and disposal life cycle stages hereafter.

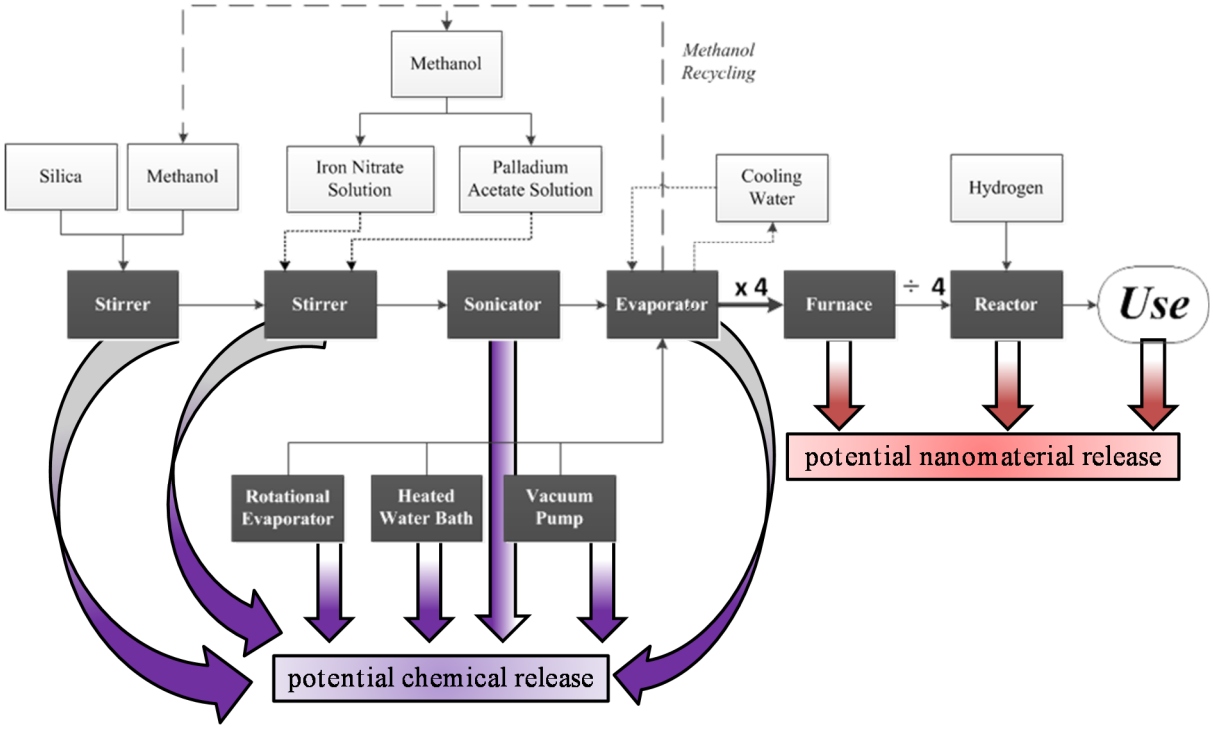


Figure 5-2 Potential chemical and nanomaterial exposure pathways across the life cycle

The impacts of such large scale release of nanoparticulate of this nature are not yet well documented. However, in addition to recognised catalytic applications of nano-iron, it is presently amongst the most widely adopted nanomaterial being used at commercial scales. Nano-iron exhibits positive effects in soil remediation for the treatment of chlorine-based compounds, pesticides, heavy metals, organic and other potential harmful contaminants (Zhang 2003), and despite a degree of uncertainty nano-iron cause no ill effects on crop growth (Barrena *et al.* 2009). Proposed future benefits of nano-iron exploitation include the removal of arsenic from drinking water (Yavuz *et al.* 2006). Some studies show negative effects on human and other animal cells, nonetheless, no conclusive outcomes have been presented. Material handling and safety sheets treat nano-iron similarly to its bulk counterparts; categorising the material as largely benign substance.

Nano-palladium is of a more pressing concern when considering implications of possible releases. Known dangers in the handling of nano-palladium include a high degree of flammability, and a known respiratory and skin irritant. Investigating further nano effects, Hildebrand *et al.* (2010) conducted worst-case scenario models for the release of palladium-iron based catalysts for waste water treatment, their results showed

little or no impact on the health of mammal and fish cells exposed ; this study also noted the tendency for these particles to agglomerate – via weak Van der Waal forces – to produce larger particle sizes and a tendency to fall out of solution as sediment, limiting the extent of any environmental release.

Much of the potential effects are likely to be mitigated by the fact that the nanoparticles are fused to their silica supports, this a fixed bond that is highly unlikely to be broken during the use of the catalysts. The operation of the catalysts also occurs within a closed system, non-dispersive in nature, and only likely to carry risks at the disposal stage of the life cycle. Additional nano-specific risk mitigation is that the silica is in varying particle sizes, mean ~50 µm, appreciably no longer a nanomaterial by definition, and at thus scale carrying no toxicity concerns.

There are uncertainties regarding the potential environmental and human health impacts attributable to nano iron and nano palladium. Indeed, in light of the benefits perceived in remediation and waste treatment, there may be an argument that the release of these nanoparticles could result in positive environmental impacts. However, long term and high concentrations of their release have not been measured, and thus many 'unknown unknowns' exist. More work is necessary, and indeed is ongoing (Safi and Berret 2010; Gottschalk and Nowack 2011), to determine the potential hazards that may arise from their release into the environment, intentionally or otherwise.

5.6 Fe-Pd Catalysis formation: results and discussion

5.6.1 *Characterised life cycle impact assessment*

When reporting the environmental impacts of the processes, it is imperative to present characterised impacts, void of influence from temporal or spatial factors; this data is most of use to others wishing to compare materials to those presented in this chapter. Table 5-6 has the overall characterised impact values for the different formed catalysts as formed during the laboratory practices. Table 5-6 has highlighted impact category titles, this is an indicator of instances where palladium metal content is the most influential factor, and occurs when the iron only catalyst is < 20 % the impact of the highest loaded palladium catalyst. This condition occurs for half of all impact categories, and can be considered to still be significant for the remainder of the categories. A better

appreciation of metal content can be seen in Figure 5-3, which accompanies that shown inTable 5-6, providing the proportional contribution of impacts between the:

- Chemicals
- Electricity
- Infrastructure
- Metal content

With progressive increases of palladium a shifting from the furnace electricity impacts to the catalyst constituent materials being the most influential, across all impact categories can be seen in Figure 5-3. A mere 1% increase in palladium catalyst loading results in the immediate shift to catalysts constituent metals being major impacts, across the majority of impact categories.

The burden of the other (non-metal) synthesis chemicals are only marginally impactful for the water depletion category, owing to the fact that cooling water is used during the condensing of the methanol evaporate. The effects of infrastructure are noticed for their metal depleting effects, predominantly due to the construction of the infrastructure equipment, this becomes a relatively less visible impact with increasing palladium metal content in the final catalyst. In Figure 5-3 an exception occurs, whereby an impact other than metal content or electricity is dominant. Seen for ozone depletion impacts, the reason is due to the diminutive measured quantitates for this category, with $\times 10^{-7}$ kg ozone depletion scores. Small values, result in smaller contributions from infrastructure having a more measurable overall impact. The ozone depletion impact is dominated, with in excess of 96 %, from the use of the vacuum pump. The presence of high fluorinated plastics and PTFE, is necessary for laboratory equipment to be resistant to a wide range of chemical attack, foreseeably, improved and bespoke synthesis pathways for the catalysts in isolation could justify the removal of fluorine contain elements due to the relatively benign nature of the chemicals used in the Fe-Pd catalysts under investigation.

Table 5-6 Characterised impacts, using ReCiPe midpoint methodology for the formation of the different catalysts. Bars compare synthesised catalysts across specific impact categories.

	Fe20	Fe10Pd1	Fe20Pd1*	Fe30Pd1	Fe40Pd1	Pd1Fe20*	Pd2Fe20	Pd3Fe20	Pd4Fe20
Climate change kg CO_2 eq	6.6E-01	8.3E-01	7.2E-01	6.2E-01	5.2E-01	7.2E-01	7.8E-01	8.4E-01	9.0E-01
Ozone depletion kg CFC-11 eq	9.7E-07	1.1E-06	9.6E-07	8.1E-07	6.7E-07	9.6E-07	9.6E-07	9.5E-07	9.4E-07
Human toxicity kg 1,4-DB eq	1.4E-01	4.6E-01	4.3E-01	3.9E-01	3.6E-01	4.3E-01	7.1E-01	9.9E-01	1.3E+00
Photochemical oxidant formation kg NMVOC	1.3E-03	4.6E-03	4.3E-03	4.0E-03	3.7E-03	4.3E-03	7.3E-03	1.0E-02	1.3E-02
Particulate matter formation kg PM10 eq	6.5E-04	8.2E-03	7.8E-03	7.4E-03	7.1E-03	7.8E-03	1.5E-02	2.2E-02	2.9E-02
Ionising radiation kg U235 eq	2.8E-01	3.5E-01	3.1E-01	2.6E-01	2.2E-01	3.1E-01	3.4E-01	3.7E-01	4.0E-01
Terrestrial acidification kg SO_2 eq	2.0E-03	3.9E-02	3.7E-02	3.5E-02	3.4E-02	3.7E-02	7.2E-02	1.1E-01	1.4E-01
Freshwater eutrophication kg P eq	1.8E-04	4.0E-04	3.6E-04	3.2E-04	2.9E-04	3.6E-04	5.4E-04	7.1E-04	8.9E-04
Marine eutrophication kg N eq	4.6E-04	6.1E-04	5.4E-04	4.6E-04	4.0E-04	5.4E-04	6.1E-04	6.8E-04	7.6E-04
Terrestrial ecotoxicity kg 1,4-DB eq	4.5E-05	6.2E-05	5.4E-05	4.7E-05	4.0E-05	5.4E-05	6.4E-05	7.4E-05	8.4E-05
Freshwater ecotoxicity kg 1,4-DB eq	2.9E-03	1.2E-02	1.1E-02	1.0E-02	9.3E-03	1.1E-02	1.9E-02	2.6E-02	3.4E-02
Marine ecotoxicity kg 1,4-DB eq	3.1E-03	1.2E-02	1.1E-02	1.0E-02	9.2E-03	1.1E-02	1.8E-02	2.6E-02	3.4E-02
Agricultural land occupation m^2a	1.1E-02	1.5E-02	1.3E-02	1.1E-02	9.2E-03	1.3E-02	1.4E-02	1.5E-02	1.7E-02
Urban land occupation m^2a	2.7E-03	4.4E-03	3.9E-03	3.5E-03	3.0E-03	3.9E-03	5.1E-03	6.3E-03	7.5E-03
Natural land transformation m^2	1.3E-04	1.6E-04	1.4E-04	1.2E-04	9.8E-05	1.4E-04	1.5E-04	1.6E-04	1.7E-04
Water depletion m^3	5.1E-03	8.0E-03	7.1E-03	6.2E-03	5.4E-03	7.1E-03	9.0E-03	1.1E-02	1.3E-02
Metal depletion kg Fe eq	1.3E-02	4.7E-02	4.4E-02	4.1E-02	3.8E-02	4.4E-02	7.5E-02	1.1E-01	1.4E-01
Fossil depletion kg oil eq	2.0E-01	2.6E-01	2.2E-01	1.9E-01	1.6E-01	2.2E-01	2.4E-01	2.6E-01	2.8E-01
Cumulative Energy Demand MJ	1.2E+01	1.5E+01	1.3E+01	1.1E+01	9.2E+00	1.3E+01	1.4E+01	1.5E+01	1.6E+01

Note: highlighted category titles, when difference between least and most impactful catalyst are at least 5-fold

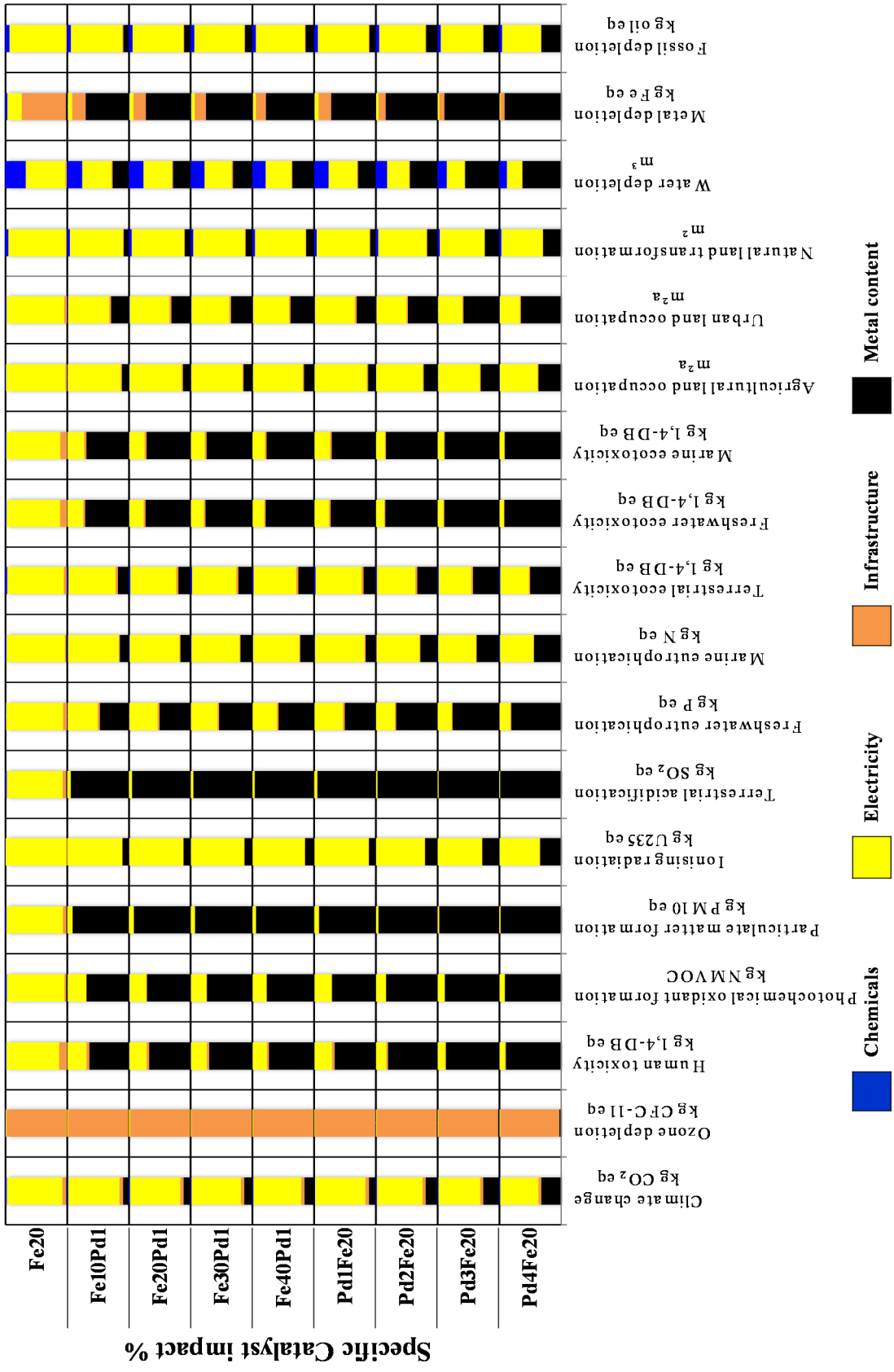


Figure 5-3 ReCiPe midpoint characterised impact, percentage breakdown of the different life cycle contributors in the formation of each catalyst

5.7 NORMALISED LCIA

In order to get a better visualisation of the contribution of different life cycle impacts in a broader context, the normalised values for the ReCiPe midpoint categories are presented in Figure 5-4 and Figure 5-5. The summation of normalised impacts across categories is useful as a comparator between different life cycle stages, allowing the relative overall impact of discrete aspects to be seen. Adopting this approach gives a wider perspective on potential impacts, shows that the vacuum pump, although still impactful amongst infrastructure devices, is of lesser concern in the context of the overall LCA results.

The mechanical stirrer is the sole example of an equipment piece with a higher embodied impact than an electricity impact for the process under investigation. To a certain extent this was due to both sonication and heating activities being high energy intense pieces of equipment, the in-use impacts therefore outweighed the initial embodied impacts.

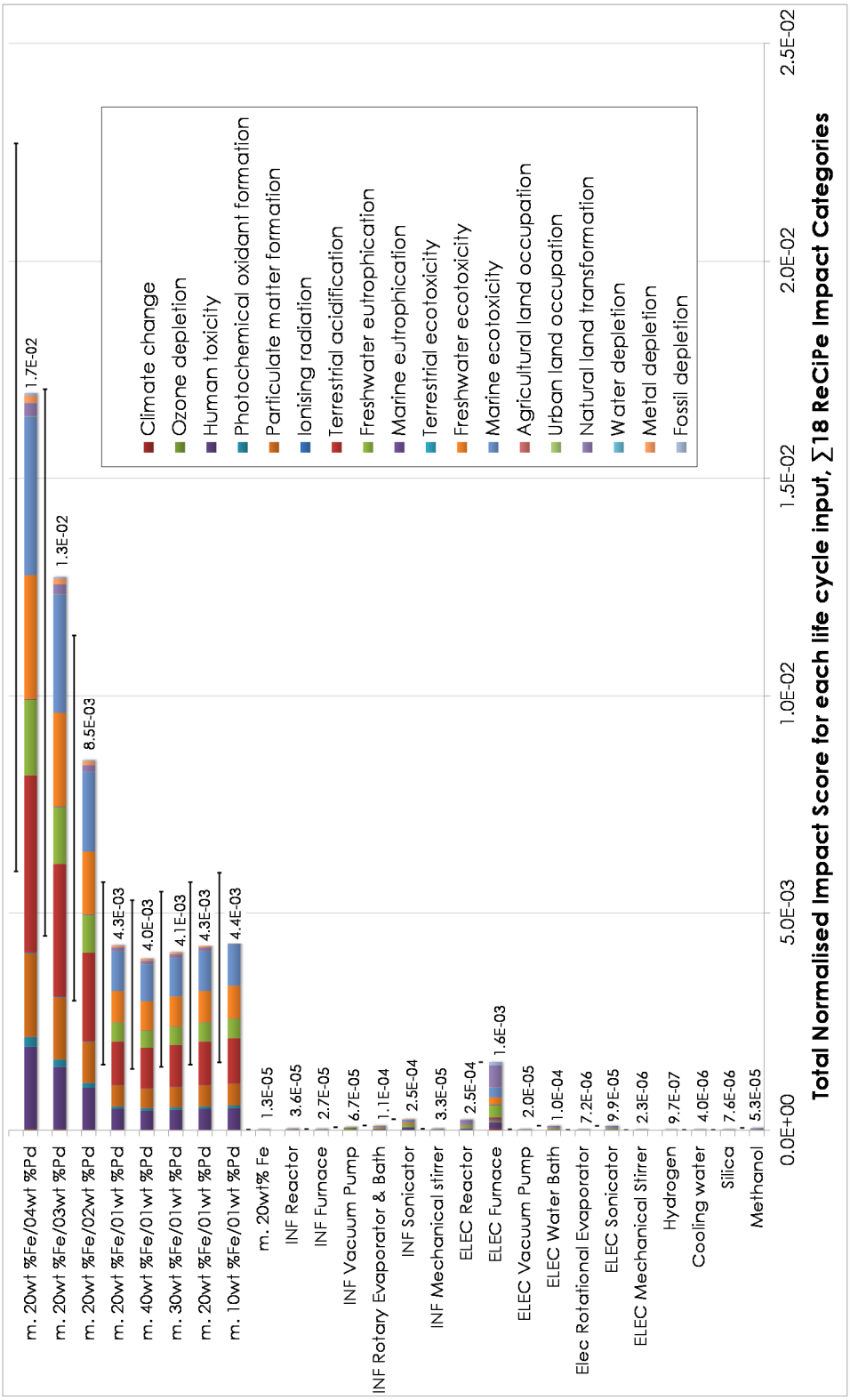


Figure 5-4 The normalised impact of the life cycle stages, the range bars shown for the catalysts are indicative of Palladium recycling rates.

All infrastructure and electricity impacts are presented for the mean catalyst formed, δm , 2.8 grams ~36% impacts.

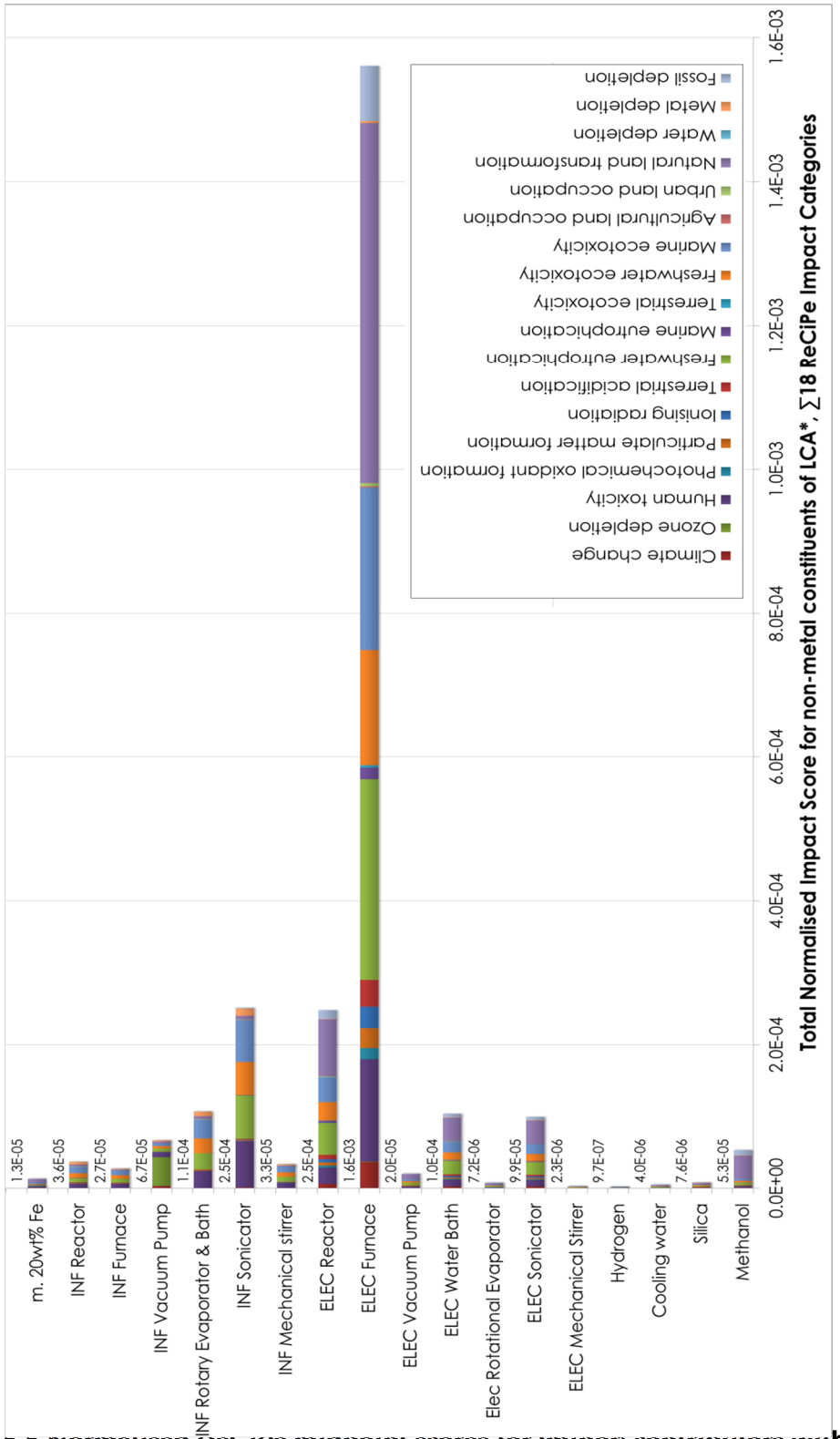


Figure 5-5 Normalised ReCiPe midpoint scores for 'minor' contributors within the system boundary i.e. all life cycle stages without palladium content. All infrastructure and electricity impacts are presented for the mean catalyst formed, δm , 2.8 grams ~36% impacts.

5.7.1 *PALLADIUM AND IRON IMPACTS*

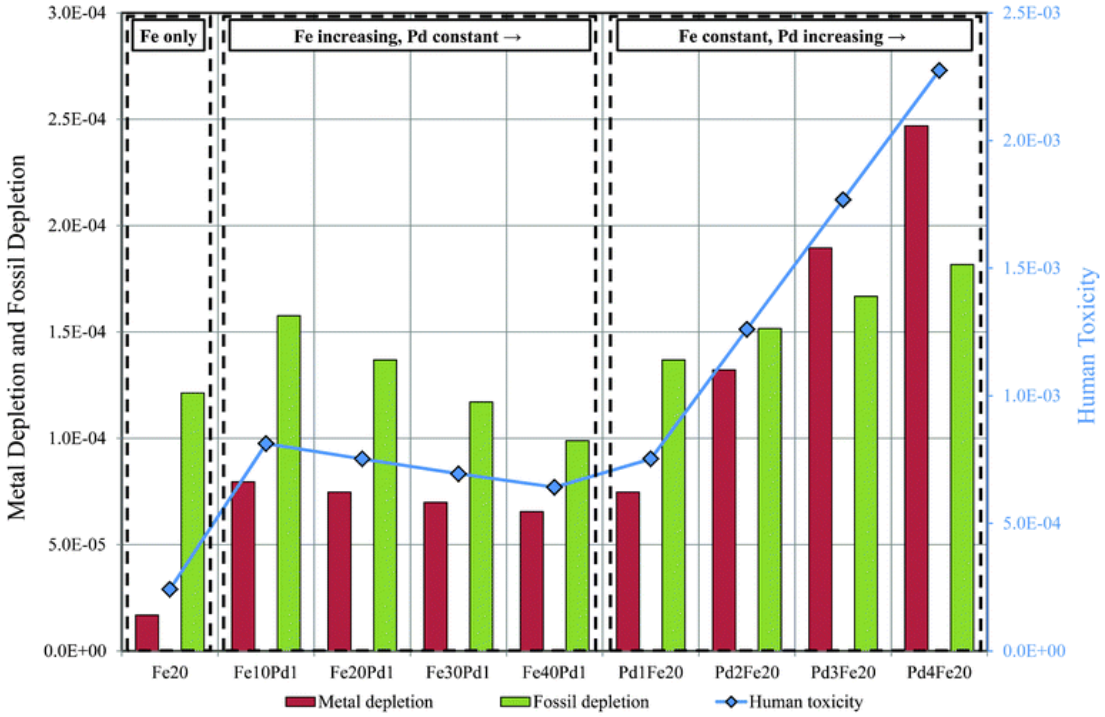


Figure 5-6 Normalised ReCiPe midpoint scores for the metal depletion, fossil depletion and human toxicity impacts of the catalysts formed. (Griffiths *et al.* 2013b)

There is a negative compound effect being witnessed for the highest loaded palladium catalysts. Firstly, the increase of iron loading between Fe10Pd1 and Fe40Pd1 'bulks' up the catalyst mass minimising the relative contribution of palladium life cycle impacts. Secondly, the increase of palladium loading from 1 to 4 wt.% leads to ever increasing witnessed impacts.

Figure 5-4 presents immediate findings that it is the chemical constituents of the catalysts, specifically palladium addition, which leads to the largest embodied impacts. Certainly, when compared to a catalyst with no palladium a relatively negligible impact score is seen. Bands of colour/impact along the catalyst bars of Figure 5-4, are nominally identically proportioned across the catalysts containing palladium, showing a near linear progression in response to palladium wt.% loading, i.e. iron loading has little or no impact on the catalyst environmental impact.

The Ecoinvent (Ecoinvent Database v2.2 2010) dataset for palladium was one that synthesised life cycle stages from the extraction and transportation of the raw material,

total mining/extraction impacts have been allocated on a mass basis of the obtained palladium metal. The proportion of recycled content of palladium used is 26%. Figure 5-4 represents the 3 and 75 % metal recycled content (RC) values in the form of error bars, showing the effect of varying palladium on the overall LCA results of this study.

Globally palladium is found in trace quantities, even the highest concentration mined have platinum group metals in the range of 3-100 ppm of the extracted ore (Renner *et al.* 2001). Once extracted, the ore is finely ground and treated with extensive quantities of acid, many times the order of magnitude of the mass of final extracted ore. Palladium ore extraction is therefore responsible for the impacts shown in Figure 4.

5.7.2 *SENSITIVITY ANALYSIS: RECYCLING RATES OF PALLADIUM*

The cradle to gate impacts of palladium-containing materials are appreciably high, as shown in Figure 5-4, as such the benefits of using secondary (recycled) palladium has very significant implications on the life cycle impacts across all measured environmental and energy use categories. When investigating the sensitivity of palladium usage, and without direct access to information from palladium producers and supple chains, it was found that few detailed life cycle inventory datasets are available for LCA practitioners. Ecoinvent (Ecoinvent Database v2.2 2010), the only source found with palladium datasets, has four datasets for palladium metal, two of which for primary or mined sources, and the remainder for recycled palladium routes.

1. Palladium, primary, Russian mine
2. Palladium, primary, South Africa mine
3. Palladium, secondary, at European refinery; the recovery of palladium from automotive catalysts, based on a German facility indicative of the Europe-wide process.
4. Palladium, secondary, at Swedish precious metal refinery; the recovery of palladium from waste electronic components, based on data from a single Swedish installation.

The range of impacts in these four modelled system was examined, and were found, as shown in Figure 5-7, to vary considerably from one another. Figure 5-7 uses Russian mine data as the reference (100%) point, and based on equal quantities of palladium from the four systems. Secondary palladium systems have considerably lower burdens than those of primary sources, effectively halving the total impact across the majority of measured impacts. On the whole, most impact categories show little difference between the impacts of Russian and South African mines. Exceptions between primary datasets exist, South African mines have massively higher human toxicity and double the freshwater eutrophication impacts. Conversely, Russian mines have higher photochemical oxidant formation, particulate matter formation, and terrestrial acidification impacts. The impact of palladium within any LCA study is thus significantly affected by the representative dataset chosen to model its usage.

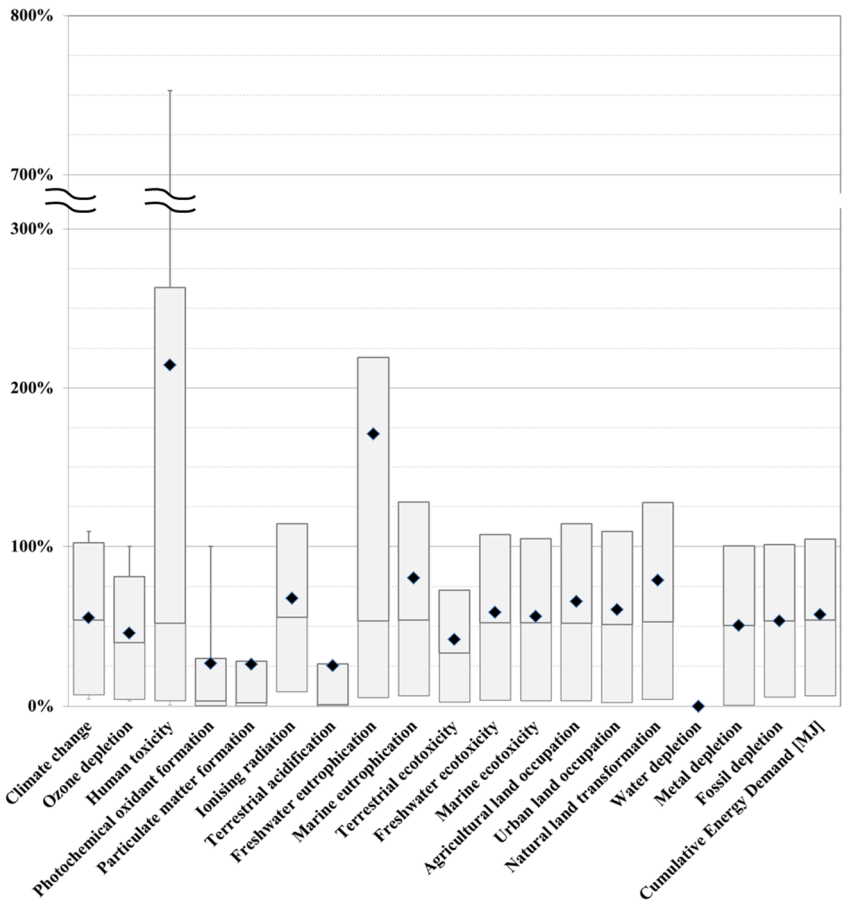


Figure 5-7 Box and whisker plot, comparing characterised ReCiPe midpoint scores for LCI datasets of palladium. Far outliers are kept within the range due to scarcity of available data.

Table 5-7 shows a range of potential palladium mixes of both primary and secondary sources. The reference Ecoinvent dataset has only 3% RC, however, this was found to be significantly lower than global average mix. Given the sensitivity of palladium,a modification of the data source occurred with 26 % RC used as a representative account of palladium global metal mix. This RC value is in agreement with many sources; (UNEP 2011) between 25 and 50%, US geological survey ~ 30% (US Geological Survey 2012), and Johnson Matthey's palladium supply-demand global market reports 26% (Johnson Matthey plc. 2012).

Breakdown of production a future 'optimistic', arguably unrealistic, scenario for a global palladium mix of 75 % RC is presented in Table 5-7, and included for academic purposes. This 75 % RC target might be overly optimistic for the foreseeable future, since year on year recycling rates have in fact dropped in recent years (US Geological Survey 2012), this is due to recovery of palladium from electronic and automotive catalysts becoming more arduous due to reduced concentration in these applications. Increased end-of-life burdens can be considered as a negative side-effect of miniaturisation/nanotechnology, whereby improved resource use in the production phase has had a knock on ill effect later down the life cycle. The challenge of end-of-life recovery of nanomaterials is discussed in chapter 2 (section related to negative potential side-effects of ENM use).

Table 5-7 Representative mixes used for the palladium inventory datasets, with differing recycled content (RC). All datasets sourced from Ecoinvent (Ecoinvent Database v2.2 2010)

	Pd mix, 3% RC	Pd mix, 26% RC	Pd mix, 75% RC
Primary, Russian Mines	**68.5 %**	**33 % + 11%***	**12.5%**
Primary, South African Mines	**28.5 %**	**29 %**	**12.5%**
Secondary / recycled	**3 %**	**26 %**	**75%**
* No datasets available for North American primary sources, Russian mine dataset has been used.			

If palladium retrieval can be improved in future recycling processes the abundance and nature of the palladium containing goods; mostly automotive catalysts (67%) and

consumer electronics (12%) and chemical and dental industry 5% (US Geological Survey 2012), have comparatively short life cycle use phases, in comparison to other traditional metals, meaning it is available for re-use and incorporation as a secondary resource input sooner.

5.7.3 *IRON IMPACTS WITHIN THE LCIA*

The impacts of iron use, in the context of this study are effectively lost in comparison to the overwhelming impacts that arise from the extraction and processing of the much rarer metal palladium. The iron is used in the form of iron nitrate, and it is indeed the nitric acid used in the formation of this compound that gives rise to the largest environmental impact; >98% across all impact categories.

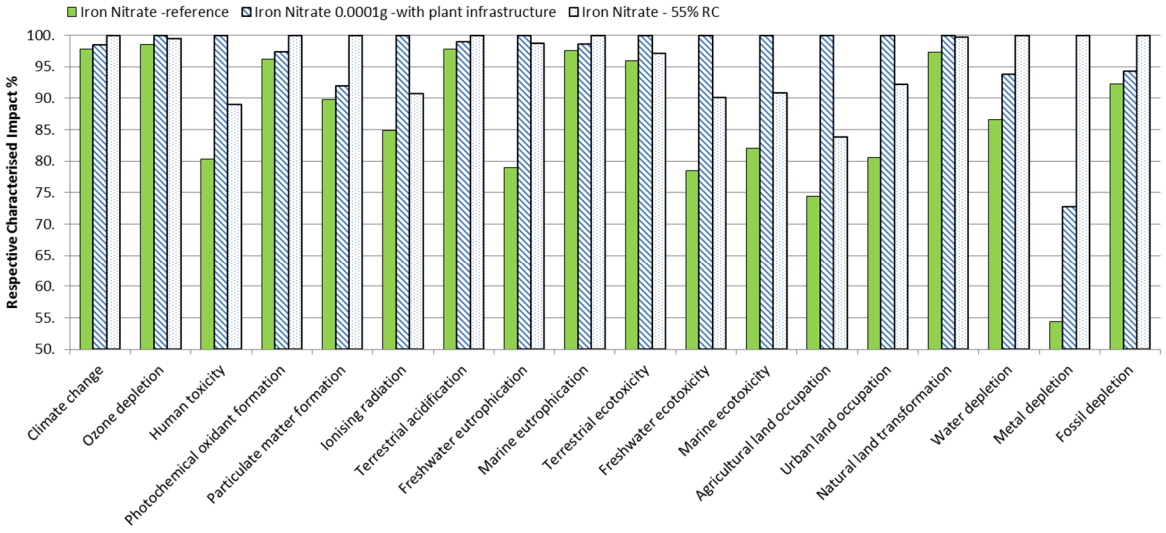


Figure 5-8 Iron nitrate modelled as: reference case (100% recycled content), including hypothetic plant infrastructure, and considering primary metal content (55% recycled content)

A representative mix of primary and secondary iron mix were modelled based on a TATA Steel report (TATA Steel INC. 2013). UK iron recycling rates of approximately 55%, the effects of recycled content in the iron nitrate are shown in Figure 5-8, apart from the metal depletion impacts there is overall little difference between 55 – 100 % RC, or whether plant impacts is modelled, and even in the cases of large discrepancies e.g. metal depletion, these have relatively negligible impacts when considering the overall life cycle impacts as shown in Figure 5-4 and Figure 5-5. The impacts of steel would

have to considerably increase before any witnessed impacts in the system under investigation to show significant changes.

5.7.4 *SCENARIO ANALYSIS: 'LEAN' LESS IMPACTFUL METAL NANOPARTICLE FORMATION AND DEPOSITION*

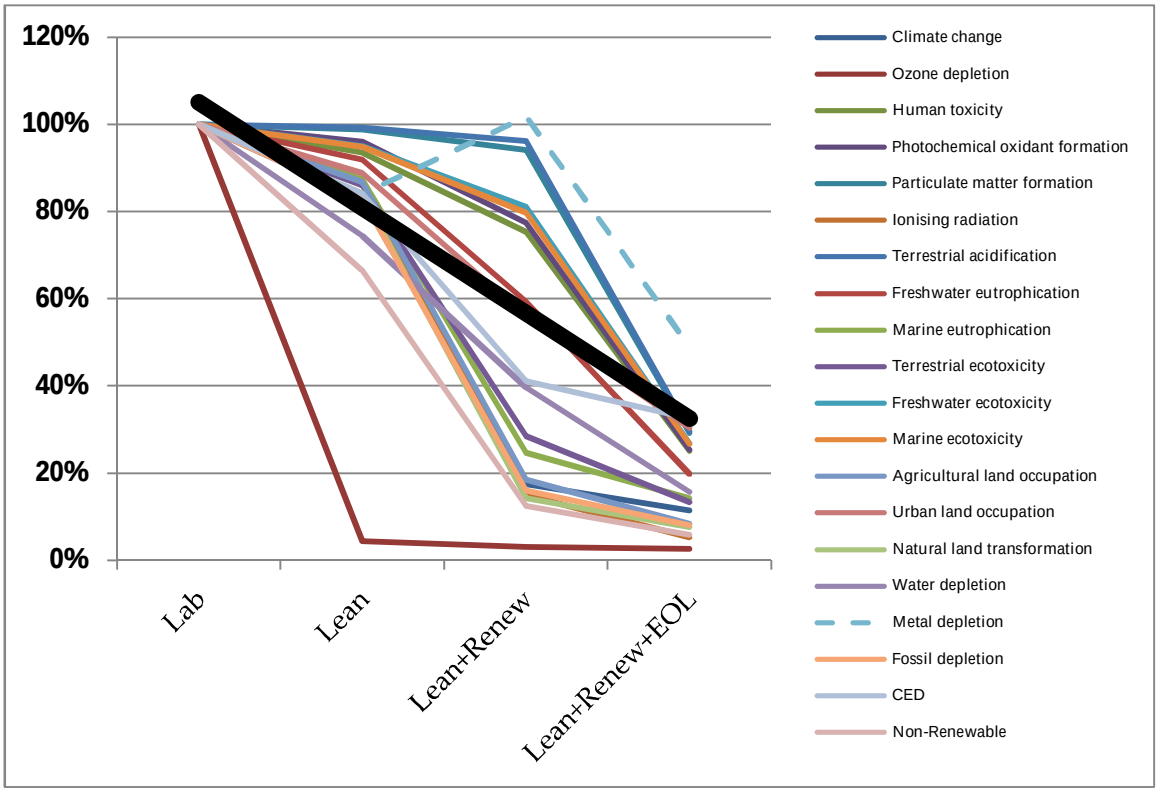


Figure 5-9 The declining impact due to more efficient synthesis process, use of renewable electricity source, and the retrieval of high impact palladium metal. Figures shown for Pd4Fe20.

When considering the life cycle burdens presented in the previous impact assessment sections of this chapter, it can be appreciated that impacts are mostly dominated by palladium, followed by electricity usage, and to a lesser extent the infrastructure embodied impacts. A few key scenario differences are introduced in the LCA assessment to see what implementable system changes could be achieved. The relative effect these changes would have are shown in and the relative effect these would have.

- Improved material/process throughput –'lean'

The allocation of impacts in the reference case is dependent on the current laboratory practices; however, if the system was to be modelled as a more 'lean setup' or continuous process a time-based allocation procedure would be appropriate. Time allocation has been conducted by relating the time invested by a piece of equipment during a specific life cycle stage to the total serviceable lifetime of that piece of equipment.

Table 5-8 Changes in impacts due to the adoption of different time-based allocation method.

	Equipment embodied impact per run		Relative allocation of infrastructure in 'lean' compared to laboratory model
	Laboratory setup	**Efficient throughput**	
Mechanical stirrer	**1.37E-4**	**2.85E-6**	**2.1%**
Evaporator	**9.13E-5**	**1.90E-6**	**2.1%**
Vacuum pump	**1.37E-4**	**2.85E-6**	**2.1%**
Sonicator	**1.37E-4**	**2.85E-6**	**2.1%**
Furnace	**2.28E-5**	**2.28E-5**	**100%**
Reactor	**5.48E-5**	**2.28E-6**	**4.2%**

Table 5-8 shows that changing the allocation to represent this more 'lean' production process, has significant effects on most of the equipment embodied impacts. Furnace impacts, however, remain the same, since two batches a day returns the same as the amount of 12 hour furnace operations that could be ran consecutively in a day.

- Removal of unnecessary stages and recycling of chemicals –'lean'

Adopting a similar perspective of producing a more streamlined process, the reactor ramp-up period is omitted from the improved modelled scenario, see Table 5-3. Additional efforts to seek where additional process enhancement when moving towards scale-up might reduce the relative infrastructure impacts were not followed, owing to that fact that at present these are of lesser pressing concerns to the dominant palladium and energy impacts. However, as previously discussed, the use of methanol and cooling water are modelled to be 90% recycled.

- Use of low-impact electricity source

The greatest mechanism for reducing the burdens of energy consumption comes from adopting a less polluting form of energy generator. In this scenario, electricity from the UK mix is substituted with that obtained from renewable wind power. A kWh of electricity then drops from being ~0.59 to 0.017 kg CO_2 eq, and shows drops across all other impact categories, with the exception of metal depletion scores which show a marginal increase from renewable wind power provision.

- End-of-life precious metal recovery stage

Finally an end of life metal recovery of palladium metal is conducted. Just as the metals are introduced as solutes, through the use of acid it has been hypothesised that the deposited metal nanoparticles can be retrieved from the silica substrates; for re-use within the same application or re-introduced into the global mix.

The dissolution of palladium occurs in a solution of aqua regia, a 3:1 mix of hydrochloric acid and nitric acid, agitated within a sonicator;

$$Pd + \mathbf{2}\ NO_3 + 4H^+ \rightarrow Pd^{2+} + 2\ NO_2 + 2\ H_2O$$

$$Pd^{2+} + 2Cl^- \rightarrow PdCl_2$$

Similarly, iron is removed via treatment with nitric acid;

$$Fe + \mathbf{4}\ HNO_3 \rightarrow Fe(NO_3)_3 + NO + 2\ H_2O$$

The allocation of impact occurs via the total volume in which the laboratory 1.4 litre sonicator could process; based on the densities of the iron-palladium-silica catalysts, and the volume of acid required to achieve total dissolution. Accounting for impurities and other bodies that might react with the acid, an additional 20% of acid volume above stoichiometry was modelled. Additionally only 70% of the metal was assumed to be recoverable via this process; a figure deemed achievable accounting for loses and practically irretrievable material fused more strongly to the silica substrate. Sonication is modelled to last for 1 hour, and is modelled using the UK electricity grid mix and the renewable wind mix respectively.

5.7.5 *Fe-Pd Catalyst Synthesis cradle-to-gate improvements*

A significant reduction across all impacts is possible through the implementation of enhanced process throughput, increased recycled content of palladium and a switch to a lower impact renewable electricity source, this is shown with relation to the reference case in Table 5-9.

Impacts attributable to palladium metal content remain the most dominant in the improved scenario, showing the least reduced impact in comparison to the higher loaded iron catalysts.

Metal and water depletion impacts buck the trend of lower-palladium higher-iron catalysts. Although still a greater impact overall, the proportional increase of recycled metal content lowers the relative impact of these catalysts in comparison to the reference case systems. The higher metal extraction impacts of a wind power dataset are also being felt by the lower-loaded catalysts, which due to their relatively low impact in this category compared to the higher palladium loadings, are displaying adverse cradle-to-gate effects.

Table 5-9 The effects of improving the life cycle impacts . Resultant impact as a proportion of current measured system. All units in percentage (%)

	Fe20	Fe10Pd1	Fe20Pd1*	Fe30Pd1	Fe40Pd1	Pd1Fe20*	Pd2Fe20	Pd3Fe20	Pd4Fe20
Climate change	4.6	5.8	7.2	9.0	11.4	7.2	9.4	11.3	12.9
Ozone depletion	2.2	2.3	2.4	2.5	2.5	2.4	2.6	2.8	3.0
Human toxicity	9.5	22.8	23.5	24.1	25.1	23.5	26.1	27.3	27.9
Photochemical oxidant formation	5.8	22.3	23.2	24.1	25.4	23.2	26.0	27.3	27.9
Particulate matter formation	8.2	28.4	28.7	28.7	29.3	28.7	29.2	29.6	29.6
Ionising radiation	0.9	3.8	4.2	4.6	5.2	4.2	6.8	9.0	10.8
Terrestrial acidification	7.0	29.1	29.3	29.2	29.7	29.3	29.5	29.8	29.7
Freshwater eutrophication	4.8	16.9	17.7	18.5	19.8	17.7	21.8	24.0	25.2
Marine eutrophication	5.7	7.9	9.6	11.6	14.1	9.6	12.4	14.6	16.4
Terrestrial ecotoxicity	5.5	9.3	10.4	11.7	13.4	10.4	13.7	16.2	18.0
Freshwater ecotoxicity	12.9	25.3	25.8	26.1	26.9	25.8	27.5	28.3	28.6
Marine ecotoxicity	12.9	25.0	25.5	25.9	26.7	25.5	27.3	28.2	28.5
Agricultural land occupation	3.1	5.8	6.5	7.3	8.4	6.5	9.1	11.3	13.0
Urban land occupation	29.4	29.6	29.8	30.0	30.4	29.8	29.8	29.9	29.9
Natural land transformation	2.8	4.5	5.3	6.3	7.6	5.3	7.4	9.3	10.9
Water depletion	7.2	13.2	13.9	14.6	15.7	13.9	17.5	19.9	21.5
Metal depletion	108	54.2	52.6	50.6	49.0	52.6	42.9	39.1	36.9
Fossil depletion	3.3	5.5	6.1	6.9	8.0	6.1	8.4	10.4	12.0
CED	31.9	31.7	31.9	32.1	32.5	31.9	31.8	31.7	31.6

NOTE * *same catalyst, different nomenclature to show changing iron and palladium impacts respectively. Orange cells indicate where the least improvement has been witnessed, and blue the greatest improvement.*

5.8 SPECIFIC IMPACTS

Table 5-10 Comparative GHG, Cumulative Energy and ReCiPe Endpoint impacts of the catalysts formed

1 g of Material	Embodied Carbon $kgCO_2eq$	Embodied Energy MJ	ReCiPe Endpoint Scores		
			Human Health DALY	Ecosystem Damage Species.yr	Resource Depletion $
Cat_Fe_20	0.655	11.65	1.20E-06	5.47E-09	3.25
Cat_Fe10_Pd1	0.826	14.84	3.62E-06	7.15E-09	4.12
Cat_Fe20_Pd1*	0.719	12.85	3.34E-06	6.24E-09	3.57
Cat_Fe30_Pd1	0.616	10.95	3.07E-06	5.37E-09	3.04
Cat_Fe40_Pd1	0.523	9.22	2.83E-06	4.58E-09	2.56
Cat_Fe20_Pd1*	0.719	12.85	3.34E-06	6.24E-09	3.57
Cat_Fe20_Pd2	0.779	13.98	5.48E-06	6.98E-09	3.87
Cat_Fe20_Pd3	0.84	15.15	7.61E-06	7.74E-09	4.18
Cat_Fe20_Pd4	0.901	16.3	9.74E-06	8.49E-09	4.49
Aluminium, primary	0.012	0.194	2.71E-08	1.03E-10	0.05
Copper, primary	0.002	0.034	4.93E-08	2.07E-11	0.01
Gold, primary	18.6	312.8	4.51E-04	2.32E-07	104
Palladium, primary	10.6	210.3	9.61E-05	9.94E-08	52

Table 5-10 presents a summary of environmental burdens associated with the synthesis of the different catalyst. In the context of the catalytic route for CO_2 utilisation the embodied carbon values are of use, in transformation of CO_2 into fuels again the embodied energy is also something that requires consideration. ReCiPe endpoint scores are essentially summarised and weighted versions of the majority of the 18 midpoint categories detailed in the LCIA of this work, included for quick comparison between catalysts. The inclusion of 'classic' materials in Table 5-10 provides a frame of reference in interpretation the relative impacts of the formed catalyst, found to be many orders greater than aluminium and copper, however, significantly lower than palladium metal and more so for gold.

If the system boundary were to be modelled in accordance to the implementable changes presented in the scenario analysis, section 5.7.4, then the resultant impact as a proportion of the reference system is presented in Table 5-11.

Table 5-11 The footprint as a percentage of the values shown in Table 5-10, should process changes, as those suggested in 'lean+renew+EOL' scenario analysis be implemented.

1 g of Material	Embodied Carbon $kgCO_2eq$	Embodied Energy MJ	ReCiPe Endpoint Scores		
			Human Health DALY	Ecosystem Damage Species.yr	Resource Depletion $
Cat_Fe_20	5%	32%	6%	5%	9%
Cat_Fe10_Pd1	6%	32%	**21%**	**9%**	**11%**
Cat_Fe20_Pd1*	7%	32%	**22%**	**10%**	**13%**
Cat_Fe30_Pd1	9%	32%	**23%**	**11%**	**12%**
Cat_Fe40_Pd1	11%	**33%**	**24%**	**13%**	**13%**
Cat_Fe20_Pd1*	7%	32%	**22%**	**10%**	**13%**
Cat_Fe20_Pd2	9%	32%	**25%**	**13%**	**14%**
Cat_Fe20_Pd3	11%	32%	**27%**	**16%**	**17%**
Cat_Fe20_Pd4	13%	32%	**28%**	**18%**	**18%**

5.9 IRON –PALLADIUM NANOPARTICLE CATALYST CONCLUSIONS

This LCA work has resulted in a comprehensive capture of the systems and impacts during the synthesis of nanoparticle iron and palladium catalysts, produced via a wet impregnation technique. Findings will be of use to others interested in nano catalysis fields, or similar deposition techniques.

The electricity consumed in the synthesis of the materials and the palladium content of the catalysts were the two most dominant impacts. Apart from these two aspects, all other life cycle influences from the used infrastructure, chemical constituents and even iron content of the catalysts had little or no effect. Furthermore, dependent on impact category, it is between electricity use and palladium as to the most dominant impact specific activities. In catalysts with only iron (no palladium) present, electricity becomes the omni-dominant factor of consideration Additionally, as the relative weight of palladium content increases from 1 to 4 wt % so to does the overall impact of the formed materials, and the relatively less impactful contribution from electricity use.

Through scenario analysis the potential for lower impact catalysts was explored. Enhancing the efficiency of the laboratory equipment usage sees substantial, >98%, reductions in the impacts attributable to embodied infrastructure impacts. However, palladium and energy impacts were the most important to address, the latter was

addressed by substitution of the UK grid mix model with one for renewable wind generation. The electricity substitution had the effect of reducing the ozone depletion to >5% of the reference case, with only a third of CO_2 eq emissions, fossil depletion, and ionising depletion, agricultural land occupation. Halving the marine eutrophication, terrestrial ecotoxicity and cumulative energy demand, but with lesser effects on the other impact categories.

The choice of dataset used to represent palladium in the LCA model had a high degree of influence on the overall life cycle impacts; indeed this was identified as the most sensitive of all inventory components within the system boundary. Large discrepancies lie between the proportion of primary and recycled content of palladium mix. To address this, best efforts were made to provide the most representative model, together with a range in which the palladium impacts would most likely sit within. However, despite even the best case, 75 % RC, palladium remains the most dominant impact.

To address the high burden of using palladium, a hypothetical E-O-L recovery of the metal was proposed. Using an acid treatment and sonication of the spent catalyst materials. Combining electricity and metal improvements to the model, all impacts were reduced to approximately a third of the reference vales; with all values between 3 and ~50% dependent on impact category.

Chapter 6: HETEROGENEOUS CONVERSION OF CO_2 TO HYDROCARBONS

VIA REVERSE WATER-GAS SHIFT AND FISCHER TROPSCH REACTIONS, USING NANOMATERIAL CATALYSTS

Highlights

- This chapter covers a novel reverse water-gas shift –coupled- Fischer-Tropsch (RWGS-FT) process, capable of converting CO_2 into hydrocarbons with carbon chain lengths up to C7.
- This is an extension of LCA work previously covered iron-palladium-silica (Chapter 5) and MWCNT impregnated with iron (Chapter 4); both of which act as the active catalysts.
- At the laboratory scale the catalysis process is performing environmentally unfavourably; incurring impacts some 1,000 to 10,000 more than that offset.
- Different scenarios are modelled to estimate the performance and limiting factors at industrially relevant scales of process roll-out.
- Performance is modelled in two ways: the overall ability of the operating process to offset GHG impacts, and secondly the production of hydrocarbons in comparison to existing industrial petrochemical routes.
- Increasing process scales are likely to diminish the inherent impacts, the assessed processes will very likely to become autothermal; not requiring energy input for the catalysis reaction to occur being a significant step, in addition to infrastructure impact reductions. The effects of these on the models are reflected in the environmental payback periods of the operating processes.
- In-use catalytic operation is found to be considerably more dominant than catalyst synthesis impacts.
- Greenhouse gas performances, as the initial focus of CCU applications, was the initial criteria for process optimisation. Expanding further on this the 'best'

catalytic routes in GHG terms were scrutinised across wider environmental impacts.

- In the best cases GHG impacts along with a third of other assessed impacts are offset within a decade of operation, and remainder within decades that follow. Metal depletion impacts, however, are not retrieved by adopting this catalysis route.

With specific concern to chapter 4

- Two MWCNT catalysts were tested, Fe_Dec_MWCNT and Fe@CNT. The latter, is found to be a better catalyst, combining lower gate synthesis impacts with enhanced CO_2 conversion performance as reported by O'Byrne *et al.* (2013).

With specific concern to chapter 5

- Results are demonstrative of the need for platinum group metal addition despite their higher synthesis gate impacts found from the findings of Chapter 5. Indeed, the iron-only catalyst has the poorest of all life cycle net impacts

- The best operating Fe40Pd1 catalyst had the best overall environmental performance. However for the seven other tested catalysts, the addition of increasing amounts of palladium are not continually beneficial from a net life cycle basis despite seemingly enhanced catalytic performance.

6.1 INTRODUCTION

This chapter provides quantitative measures of the life cycle environmental burdens associated with a laboratory scale process using engineered nanomaterials (ENMs) for the conversion of CO_2 into commodity hydrocarbon chemicals. This conversion is realised through coupling the reverse water-gas shift and Fischer Tropsch (RWGS-FT) catalysis reactions. This work is novel in two ways; firstly, CO_2 is used as the carbon feedstock in place of carbon monoxide (CO), only CO FT has a commercial presence to date(Takeshita and Yamaji 2008), such as the largest FT plants operated by SASOL in South Africa. Secondly, the life cycle evaluation of nanoscale catalyst materials for the FT process has not yet been carried out to date.

The environmental life cycle footprints of the catalysts were established and presented in chapters 4 and 5 of this thesis, specifically; multi-walled carbon nanotube (MWCNT) with nano-iron, and silica-bound nano-iron and palladium respectively. The composition of the catalysts and respective quantities used are shown in Table 6-1.

Table 6-1 RWGS-FT catalysts under assessment in this chapter

Name	Description / Composition	Mass Used
Fe20	**Amorphous silica (SiO_2) deposited with; 20wt%Fe**	**1.00 g**
Fe10Pd1	**Amorphous silica deposited with; 10wt%Fe / 1wt%Pd**	**1.00 g**
Fe20Pd1*	**Amorphous silica deposited with; 20wt%Fe / 1wt%Pd**	**1.00 g**
Fe30Pd1	**Amorphous silica deposited with; 30wt%Fe / 1wt%Pd**	**1.00 g**
Fe40Pd1	**Amorphous silica deposited with; 40wt%Fe / 1wt%Pd**	**1.00 g**
Pd1Fe20*	**Amorphous silica deposited with; 20wt%Fe / 1wt%Pd**	**1.00 g**
Pd2Fe20	**Amorphous silica deposited with; 20wt%Fe / 2wt%Pd**	**1.00 g**
Pd3Fe20	**Amorphous silica deposited with; 20wt%Fe / 3wt%Pd**	**1.00 g**
Pd4Fe20	**Amorphous silica deposited with; 20wt%Fe / 4wt%Pd**	**1.00 g**
Fe_Dec_CNT	**Multi-walled carbon nanotubes, *decorated* with iron nanoparticles**	**0.70 g**
Fe@CNT	**Multi-walled carbon nanotubes, with residual nano-iron *activated***	**0.40 g**

***** wt% , refers to weight loadings of materials, with respect to SiO_2***

**** same catalyst, nomenclature used to demonstrate palladium and iron loading effects***

The comparison of multiple materials for the same catalysis process affords insight into where environmental gains are present, and, perhaps more insightful, where commonalities exist for all the tested RWGS-FT catalysts. Fe@CNT (recognised later in this chapter as amongst the best performing catalyst) is further tested across a wider

range of reaction temperatures, pressures, and gas flow rates. The culmination of raw data analysis, together with the interpretation of the overall life cycle impact assessment, provides an account of the potential scale-up performance of the processes, providing guidance and recommendations on the wider implications of this work.

The work and findings of this chapter is the fusion of many pieces of LCA work covered in this thesis, shown in more detail in Figure 6-3 (page 147). The LCA work comes from earlier chapters covering the feedstock, energy, catalyst formation impacts, in addition to specific sections within this chapter relevant to RWGS-FT process operation.

6.2 SPECIFIC THESIS OBJECTIVES ADDRESSED WITHIN CHAPTER

The work of this chapter is contributing to three over-arching thesis objective:

Objective 2. Establish the life cycle impacts of the developed CCU processes , and, report on the environmental feasibility of further technology development

Objective 3. Communicate to technology developers key life cycle results for action

Objective 4. Communicate wider environmental impacts

6.3 CARBON DIOXIDE; A FISCHER-TROPSCH FEEDSTOCK

This chapter combines reference industrial processes to novel routes, although in the early stages of research and development, they are demonstrative of a technically feasible route of CO_2 utilisation. CO_2 is transformed into hydrocarbons in lengths of up to and including C7, or heptane. Hydrocarbons of this length can be appreciated to reside within a desirable band for societal needs(Griffiths *et al.* 2013b); encompassing natural gas, transportation fuels and feedstocks used in the pharmaceutical industry; a considerable portion of crude oil petrochemical refinery as shown in Figure 6-1.

This work considers the production of these fuels, pharmaceuticals and chemical building blocks *via* the novel ENM catalysis routes. Expanding from the performance within the laboratory to consider the possibility of implementing renewable and enhanced process operation and other efficiency means. The assessment of the processes covered in this chapter offer an academic and industrial insight into an opportunity for carbon-neutral, or at least less environmentally harmful, petrochemicals.

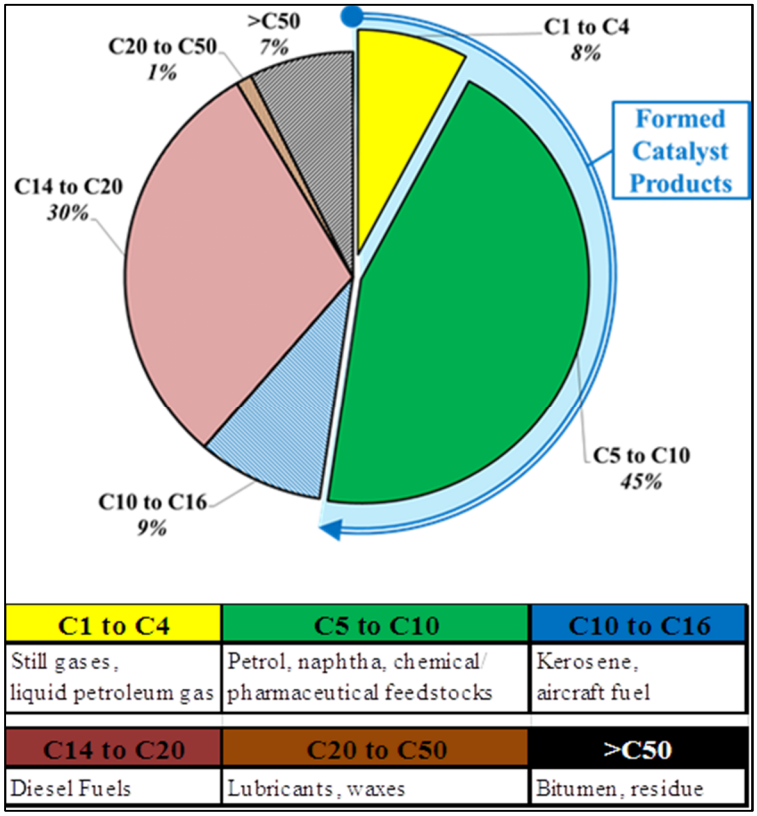


Figure 6-1 The mass split of products formed from a typical crude oil refinery process, adjusted from (EIA 2013) The catalytic process in this investigation produces compounds in ranges from C1 to C7 (Griffiths *et al.* 2013b).

6.4 OVERVIEW OF CO_2 CONVERSION ROUTE

The water-gas shift (WGS) reaction was first utilised in the 18th century by Italian physicist Felice Fontana, a process initially devised for hydrogen synthesis from water and carbon monoxide. This process is reversible, and is the necessary first step in the conversion of CO_2, through intermediary CO, into hydrocarbons.

Equation 6-1: The reverse water-gas shift reaction

Carbon Dioxide + Hydrogen $\overset{Catalyst}{\longleftrightarrow}$ Carbon Monoxide + Water

$CO_2 + H_2 \overset{Catalyst}{\longleftrightarrow} CO + H_2O$

The Fischer-Tropsch process is a long standing industrial pathway for liquid fuel production from other carbonaceous sources, such as coal or biomass (Dry 2002; Davis 2005). The feedstock of this process is H_2 and CO rich feeds, syngas, which in a temperature controlled environment and in the presence of a catalyst react to form a

range of hydrocarbons; the goal is to maximise the conversion and selectivity towards the more valuable commodity chemicals.

Equation 6-2: Fischer Tropsch Process

Hydrogen + Carbon Monoxide $\xrightarrow{Catalyst}$ Hydrocarbons + Water

$(2n+1).H_2$ + n.CO $\xrightarrow{Catalyst}$ $C_nH_{(2n+2)}$ + $n.H_2O$

(Where n denotes an integer value)

Both catalyst reactions (Equation 6-1 and Equation 6-2) are considered to occur simultaneously on the surface of the same catalyst, henceforth the process reaction is referred to as the reverse water-gas shift with Fischer-Tropsch (RWGS-FT), this overall reaction is shown in Equation 6-3. Transition metal catalysts, *via* a mechanism of charge transfer to the hydrogen atoms are theoretically capable catalysts for this process (Rofer-DePoorter 1981). However, the border group of metals consisting of manganese, iron, cobalt, nickel, rhodium, palladium and platinum have had the greatest reported success as reported by Van Der Laan and Beenackers in a literature review on the kinetics of F-T catalysis (Van Der Laan and Beenackers 1999).

Equation 6-3: The reverse water-gas shift reaction coupled with the Fischer Tropsch process.

Carbon Dioxide + Hydrogen $\xrightarrow{Catalyst}$ Hydrocarbons + Water

$n.CO_2$ + $(3n+1).H_2$ $\xrightarrow{Catalyst}$ $C_nH_{(2n+2)}$ + $2n.H_2O$

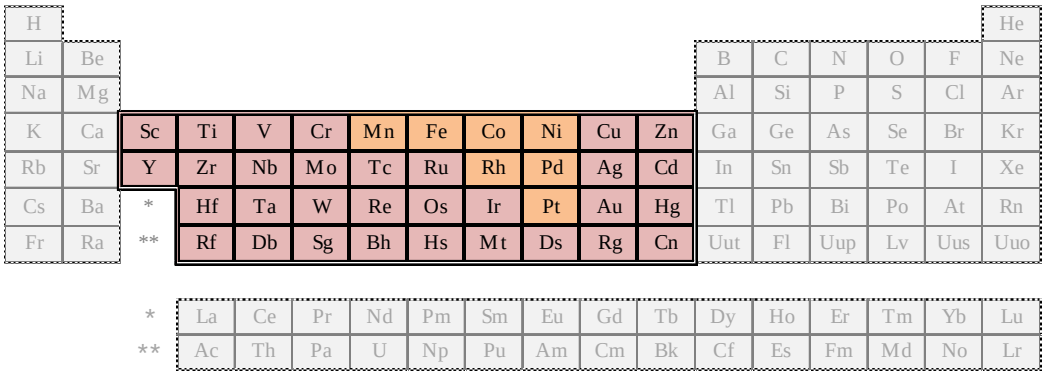


Figure 6-2 Transition metals, and those identified as capable RWGS-FT catalysts (in peach).

Certain transition metals are well proven catalysts for the RWGS-FT process (Van Der Laan and Beenackers 1999), however, it is anticipated that the exploitation of increased nano-scale reactivity (Nanda *et al.* 2003) and reduced usage of catalyst materials will provide two-fold environmental gains: better performing CO_2 conversion and hydrocarbon production, and a reduced use of mined metal reserves; LCA in this chapter quantifies any potential for favourable environmental gains.

6.5 SYSTEM BOUNDARY FOR RWGS-FT PROCESS

The RWFS-FT LCA work covers the impacts associated with the operation and upstream emissions of the processes involved in the production of hydrocarbons formed *via* the process, i.e. all stages necessary in the formation of the obtained gaseous and liquid products of the reactions. The system boundary for this process is shown in Figure 6-1.

The methodology and assumptions taken are in-line with those detailed within chapter 3, however, additional process-specific methodological approaches are detailed throughout this chapter, especially in the section 6.7 of this chapter.

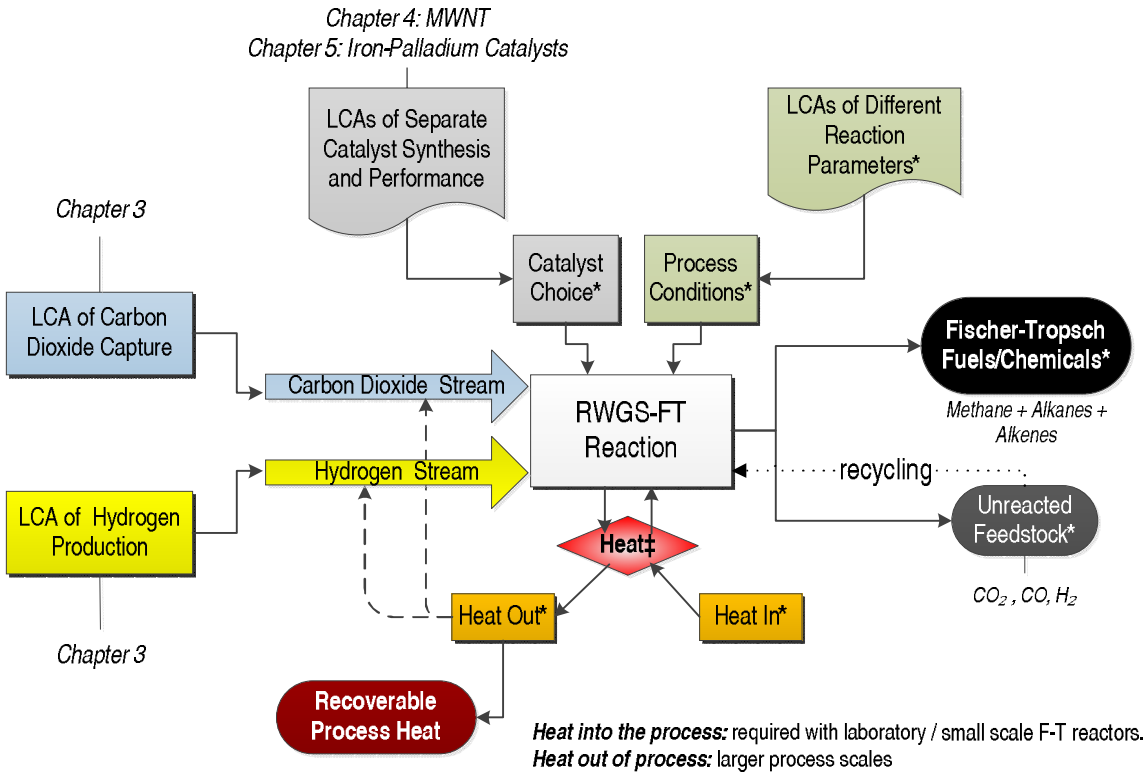


Figure 6-3 Overview of the LCA work related to the RWGS-FT

(*these activities are covered in this chapter)

The system boundary remained unchanged for all conducted LCA work. However, within the reactor itself two distinct parameters were varied for the meaningful assessment of the RWGS-FT process under investigation:

- Firstly, the choice of catalyst, either selecting one of the eight iron:palladium:silica catalysts or one of two MWCNT-iron catalysts.
- Secondly, the catalyst reactor operating conditions were varied. The catalysts were all initially tested at ambient, 1 bar, reaction pressure. This allowed a comparative assessment for the performance of all catalysts to be established. Subsequent reactions were conducted for the iron activated MWCNT, Fe@CNT, catalyst in isolation. Fe@CNT performance was measured whilst subjected to different reactor:
- temperatures; 310 to 410 °C,
- pressures; 1 bar to 12.5 bar, and
- flowrates[5]; 2 to 16 sccm (standard cubic centimetres per minute).

6.6 FUNCTIONAL UNIT

All processes are assessed on the sum-combined total of Fischer-Tropsch (FT) products formed per hour of catalysis process. Unit = mg/h. That is, the gate impact of forming the FT-products per hour of operation, unless otherwise stated.

Within this measure will be the combination of the CO_2 locked into the formed FT product per hour, the avoided impacts of forming this amount of hydrocarbons traditionally sourced 'from the well', and finally and where applicable, the consideration of exothermic heat generation as a co-product with potential utilisation for power generation; thus offsetting current grid embodied impacts.

The cross-comparable, per hour, measure for the different assessed in-situ catalysts, are of specific of interest to the technology developer, however this is supplemented with more contextual wide-ranging functional units, of:

[5] Feedstock flows by volume are 1 part carbon dioxide to 3 hydrogen, e.g. for 8 sccm; 2 CO_2 and 6 H_2.

- equivalent unit mixture of FT products formed by the catalysts; appreciably different dependent on the catalyst choice and specific reaction conditions. For comparison with alternative product pathways.

- meeting GHG neutral operating conditions. For an understanding of the effect of carbon capture and utilisation performance on other environmental indicators.

6.7 PROCESS INVENTORY DATA

A series of distinct, yet inter-linked, parameters require analysis to establish the holistic life cycle performance of the RWGS-FT process, as shown in Figure 6-4. These underpin the understanding of overall impacts of forming hydrocarbon products, to establish whether the process, in the context of CO_2 utilisation, offers any potential net GHG / wider environmental benefit.

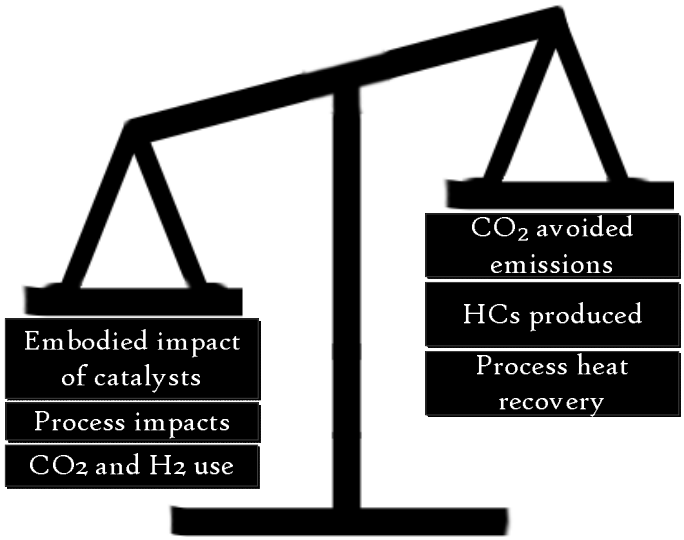


Figure 6-4 Balancing elements for the environmental performance of the process

Work from previous chapters, see Figure 6-3, provides much of the required input data:

- impacts in capturing CO_2 from flue gases of fossil fuel power plants, ***chapter 3***

- hydrogen gas feedstock use, average production mix and renewable electrolysis route ***chapter 3***

- embodied impacts of the Multi-Walled Carbon Nanotube (MWCNT) based catalysts, and the iron:palladium:silica catalysts, ***chapter 3 and 4 respectively***.

Table 6-2 provides an overview of the additional life cycle activities and inputs requiring consideration, to produce the RWGS-FT process-specific inventory data models and assumptions.

Table 6-2 Assumptions and model parameters for the different inventory data

Relevant section	
6.7.1	Process infrastructure impacts
6.7.2	Operational impacts the variations of changing reaction conditions
6.7.3	Modelled impact of different reaction conditions
6.7.4	Quantity of products formed, and CO_2 converted
6.7.5	Exhaust gas recycling for additional catalyst passes
6.7.6	*Ideal* catalyst performance; conversion and selectivity towards HCs.
6.7.7	Electricity production from generated reaction heat.
6.7.8	Catalyst operational lifetime
6.7.9	Catalyst embodied impact: re-cap from chapter 3 and 4.

6.7.1 *PROCESS INFRASTRUCTURE*

The processes are all based on laboratory components, the layout of which is shown in Figure 6-5. Much of the equipment is common to that used in the synthesis of MWCNTs, covered in chapter 4, thus related inventory data is already present for material constituents and operational lifetimes of the infrastructure. Devices such as the horizontal reactor, and gas flow controllers can be considered versatile laboratory toolkits, their operation is highly flexible and tailorable to specific tasks such as material synthesis of catalysis reaction, however, this therefore means that their operation and construction are not best optimised for specific tasks in isolation, as would be the case at advancing scales of pilot and larger industrial setups. To account for the effects of the embodied impacts of catalysts and laboratory infrastructure are disaggregated in much of the results.

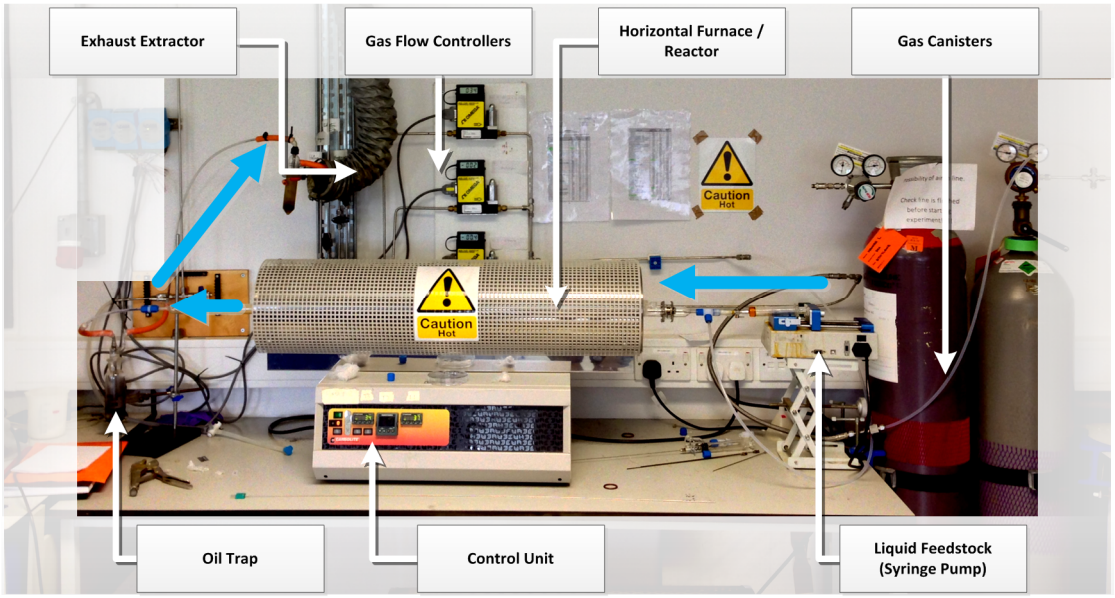


Figure 6-5 Laboratory Equipment used for the RWGS+FT process of CO_2 conversion to hydrocarbons. Blue arrows indicate the -product flow.

Moving from the laboratory, as will be shown later in this chapter, the effects of increasing scales and improved process efficiency and intensity of operation have also been explored. Modelling the take-back and material recovery of the major; metals and glass constituents are undertaken, to effectively retrieve some of the embodied environmental impacts inherent in the infrastructure equipment used.

6.7.2 *OPERATIONAL CONDITIONS*

The operational impacts refer to the effort required to sustain specific reaction conditions. Once inside the reactor, two-distinct phases occur, as shown in Figure 6-6. Initially, each catalyst is chemically activated by undergoing a pre-treatment hydrogenation phase, either the hydrogen flowrate, H_2F1, or pressure, P1, are varied. After pre-treatment the catalysts were operated at steady-state, under specific hydrogen flows, H_2F2, carbon dioxide flows, CO_2F2, reaction pressure, P2, and temperature, T2, conditions for the duration of the in-use reaction phase. The complete range of tested reactor conditions are shown in Table 6-3.

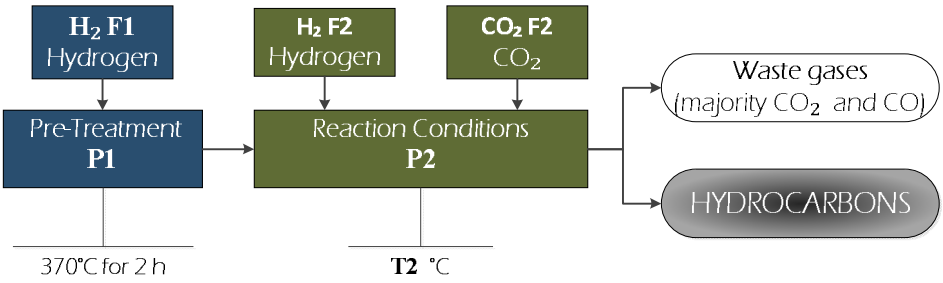


Figure 6-6 Outlining the changed conditions for the RWGS-FT catalyst reactor.

Table 6-3 Reactor conditions for the different RWGS-FT reactions

			Pre-Treatment			Reaction			
Catalyst Reactor Process Conditions			Temperature (°C)	Pressure (bar)	H_2 Flow (sccm)	Pressure (bar)	Temperature (°C)	H_2 Flow (sccm)	CO_2 Flow (sccm)
			T1	P1	H_2 F1	P2	T2	H_2 F2	CO_2 F2
Ambient Pressure:			**370**	**1**	**20**	**1**	**370**	**6**	**2**
1	**Temperature [°C]**	**310**	370	5	20	5	**310**	6	2
2		**330**	370	5	20	5	**330**	6	2
3		**350**	370	5	20	5	**350**	6	2
4		**370**	**370**	**5**	**20**	**5**	**370**	**6**	**2**
5		**390**	370	5	20	5	**390**	6	2
6		**410**	370	5	20	5	**410**	6	2
7	**Flow rate [sccm (cm^3 / min)]**	**2**	370	5	20	5	370	**1.5**	**0.5**
8		**4**	370	5	20	5	370	**3**	**1**
9		**8**	**370**	**5**	**20**	**5**	**370**	**6**	**2**
10		**12**	370	5	20	5	370	**9**	**3**
11		**16**	370	5	20	5	370	**12**	**4**
12	**Pressure: Pre-Treatment [bar]**	**1**	370	**1**	20	5	370	6	2
13		**5**	**370**	**5**	**20**	**5**	**370**	**6**	**2**
14		**10**	370	**10**	20	5	370	6	2
15		**15**	370	**15**	20	5	370	6	2
16	**Pressure: Reaction [bar]**	**1**	370	5	20	**1**	370	6	2
17		**2.5**	370	5	20	**2.5**	370	6	2
18		**5**	**370**	**5**	**20**	**5**	**370**	**6**	**2**
19		**7**	370	5	20	**7**	370	6	2
20		**10**	370	5	20	**10**	370	6	2
21		**12.5**	370	5	20	**12.5**	370	6	2
22	**Pressure: Pre-Treatment + Reaction [bar]**	**2 + 2.5**	370	**2**	20	**2.5**	370	6	2
23		**2 + 7.5**	370	**2**	20	**7.5**	370	6	2
24		**5 + 5**	**370**	**5**	**20**	**5**	**370**	**6**	**2**
25		**10 +7.5**	370	**10**	20	**7.5**	370	6	2
26		**10 + 10**	370	**10**	20	**10**	370	6	2
Key:	**Orange row = standard/reference ambient pressure reaction conditions,**								
	Yellow row(s) = standard/reference high pressure reaction conditions,								
	Grey cells = specific changes to high pressure reaction conditions.								

6.7.3 *MODELLING THE IMPACT OF DIFFERENT REACTION CONDITIONS*

Different reaction conditions, as outlined in Table 6-3, yield changes in CO_2 conversion and composition-mix, or selectivity, of different hydrocarbons formed, these changes are reflected in Figure 6-9. Quantifying the environmental implications for different operating: temperatures, pressures, and flow rates, are vital for holistic process environmental performance, and thus feedback to technology development. The approach for calculating the energetic requirements of the different conditions are covered in the following sections.

6.7.3.1 Temperature

Temperature is modelled both directly and theoretically. The direct measurement is taken using a connected power meter noting sustained power consumptions at the different reactor temperatures. In addition, the theoretical value of energy consumption at different conditions has been calculated, using the specific heat capacities for the different gases, and the required temperature increase from ambient conditions for each reaction condition;

Equation 6-4: $Energy = \dot{m}\, c\, dT$

The specific heat capacities, *c*, of CO_2 and hydrogen are appreciably different, and are both dependent on their absolute temperatures, these are accounted for in the inventory data produced. The average specific heat capacities are used for the gas mixtures across the determined temperature rises; e.g. between 25 and 370 °C for most conditions. The mass flow rate is a product of flow rates and gas densities, again average values across the temperature ranges are used.

6.7.3.2 Pressure

Within the laboratory the feedstock gases are stored in pre-filled vessels, with internal pressures in excess of even the highest tested 12.5 bar reaction pressures, thus no perceived effort is spent to obtain different pressure requirements. However, upstream life cycle efforts are invested in pressurising the feedstock gases, this consideration becomes more relevant when considering an industrially significant operation.

Uncertainty surrounds the pressurisation processes, and data scarcity was a barrier, therefore the efforts of reaching different reaction pressures are calculated theoretically.

The ideal gas law states that the pressure of n moles of a gas can be determined by the for a given temperature T and volume V, along with the universal gas constant R, with the relationship:

Equation 6-5: Gas pressure, $\boldsymbol{P = \frac{nRT}{V}}$

For a fixed quantity of gas, Boyle's law states the pressure and volume of the gas are proportional to one another, thus:

Equation 6-6: Final gas pressure,

$$\boldsymbol{P_2 = P_1\left(\frac{V_1}{V_2}\right)}$$

For an isothermal process, whereby no change in temperature is occurring, the external work performed on changing the volume of the gas is dependent on the volumetric change, from the initial volume (V1) to the final (V2).

Equation 6-7: $\boldsymbol{Work\ done}$

$$\boldsymbol{= \int_{V1}^{V2} P\,dV = \int_{V1}^{V2} \frac{nRT}{V}\,dV = nRTln\frac{V_2}{V_1}}$$

Power consumption is derived for the pressurised volumetric flow of gases passing through the reactor, calculated by appreciating the mechanical work required to compress the respective quantities of gas. The compressibility of the gases were considered in the model, but were of little effect for the pressures under investigation.

6.7.3.3 Flow Rate

The flow rate is modelled to occur *via* a pressure-differential, with the outlet of the reactor being at a lower pressure to the inlet conditions. The resultant power requirement to achieve a desired flow rate, Q, is:

Equation 6-8: Power

$$\mathbf{W} = \boldsymbol{Q}.\Delta\boldsymbol{P}$$

The pressure requirement can be calculated by considering the continuous steady-state gas flow, a derivative the Bernoulli equation can be used to establish the pressure differential required to achieve different flow rates:

Equation 6-9: Bernoulli relationship

$$\boldsymbol{P_1} + \frac{\mathbf{1}}{\mathbf{2}}\boldsymbol{\rho v_1}^{\mathbf{2}} = \boldsymbol{P_2} + \frac{\mathbf{1}}{\mathbf{2}}\boldsymbol{\rho v_2}^{\mathbf{2}}$$

If considering the feedstock gas is brought from a static condition, v_1=0, then the pressure differential for resultant flow velocity is given by:

Equation 6-10: Pressure differential

$$\Delta\boldsymbol{P} = \boldsymbol{P_1} - \boldsymbol{P_2} = \frac{\mathbf{1}}{\mathbf{2}}\boldsymbol{\rho v_2}^{\mathbf{2}}$$

The flow velocity, v, is governed by the cross-sectional area of the reaction vessel at hand, in this case shown in Figure 6-7, and the volumetric flowrate.

Equation 6-11: Flow velocity,

$$\boldsymbol{v} = \frac{\boldsymbol{Q}}{\boldsymbol{A}}$$

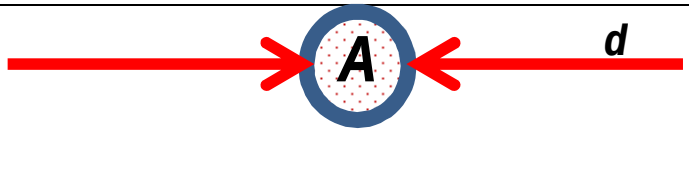
6.7.4 *ASSUMPTIONS*

The theoretical calculations for process parameter changes follow a series of assumptions, notably, that no gas leaks are occurring (this was verified in the laboratory during each run) and no thermal heat loss is occurring. Therefore, all energy put into the feedstock gas stream results in a linear corresponding pressure/flow/temperature condition. To achieve different pressure requirements, an obtainable mechanical compressor efficiency of 80 % is used, in-line with values for industrial scale compressor units (Euzen *et al.* 1993).

Reaching a 100% thermal efficiency, as calculated using Equation 6-4, for a heating device are practically unobtainable, even the most efficient thermal reactors typically do no exceed 60%. Despite this theoretical values are informative since they de-couple the specific inefficiencies of the infrastructure equipment used from the overall process results.

The additional infrastructure requirement for pressure increase have not been accounted for, this is justified for this early-scoping LCA since the likely infrastructure impacts are very likely to be negligible in comparison to the energy use for achieving pressures. Furthermore, the post-captured CO_2 is pressurised many orders of magnitude higher than any process conditions.

The impact of high pressure conditions are modelled as the additional energy required to elevate the process reactant gases from ambient to the specific gauge pressures. Additional infrastructure to achieve this pressure increase is not included in the life cycle inventory, since energy is often one of the major if not the most impactful part of an operating system's overall process impact. Further justification is considered since the CO_2 captured at the fossil fuel plant is stored at a pressure of 135 bar (Odeh and Cockerill 2008); appreciably far higher than required by the assessed reactions. The impacts of CO_2 pressurisation, as they presently stand (see chapter 3 methodology), are accounted for as part of the over-arching dataset produced for CO_2 as feedstock from carbon capture, there is danger of double-counting the efforts of pressurisation therefore. Exploring pre-pressurised post-capture CO_2 feeds would be areas for follow-up LCA assessment when moving towards realising larger RWGS-FT process scales.



d, internal diameter	**5.35**	**mm**
A, area of flow	**89.87**	**mm²**

Figure 6-7 High pressure RWGS-FT reaction vessel dimensions,

Finally, the assumptions taken for energy requirements for reaching specific reaction temperatures was not explored in more depth, predominantly since there is an expectation that the process will in fact (at industrial scales) be a net producer of heat, see section 6.7.8, and the final design of the reactor will have a very large implication on the heat exchange properties of the process (Euzen et al. 1993)

6.7.5 *HYDROCARBON PRODUCTION AND RESULTANT OFFSETS*

The catalytic conversion performance of the different catalysts at different reaction conditions are a key piece of inventory data which provide the:

- Overall quantity and composition of HC products formed. Thus allowing the determination of avoided impacts, i.e. impacts not incurred from sourcing HCs from 'the well', and the specific selectivities or bias for catalysts to form different length HCs.
- Conversion of the feedstock gases, indicating the potential for exhaust gas recycling.
- Potential process heat generation, based off quantity of formed FT product.

Figure 6-8, shows the breakdown of total hydrocarbon (HC) products formed per hour, and the CO_2 conversion – to CO and to HC – at ambient pressure, and 370 °C process conditions. Figure 6-9, considers the Fe@CNT catalyst in isolation, at the time of conducting this LCA work this catalyst was the only one being operated at different reaction conditions.

6.7.5.1 Ambient pressure RWGS-FT CO_2 conversion and Hydrocarbon production performance; for all tested catalysts

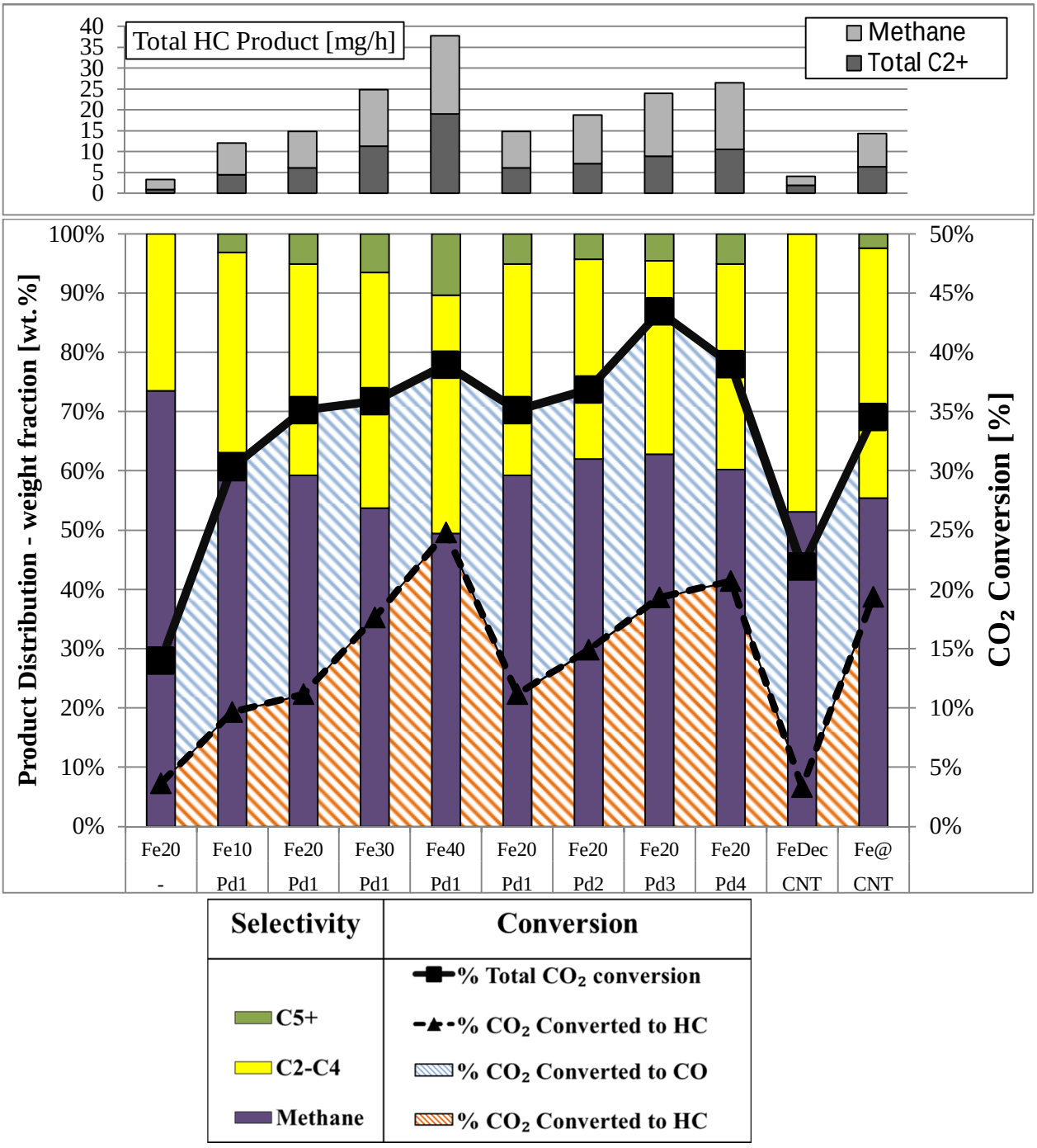


Figure 6-8 The obtainable hydrocarbon product, CO_2 conversion values and weight fraction of the different hydrocarbons formed. Data for all catalysts under standard conditions, atmospheric pressure and 370 °C

6.7.5.2 Fe@CNT performance across assessed reaction conditions

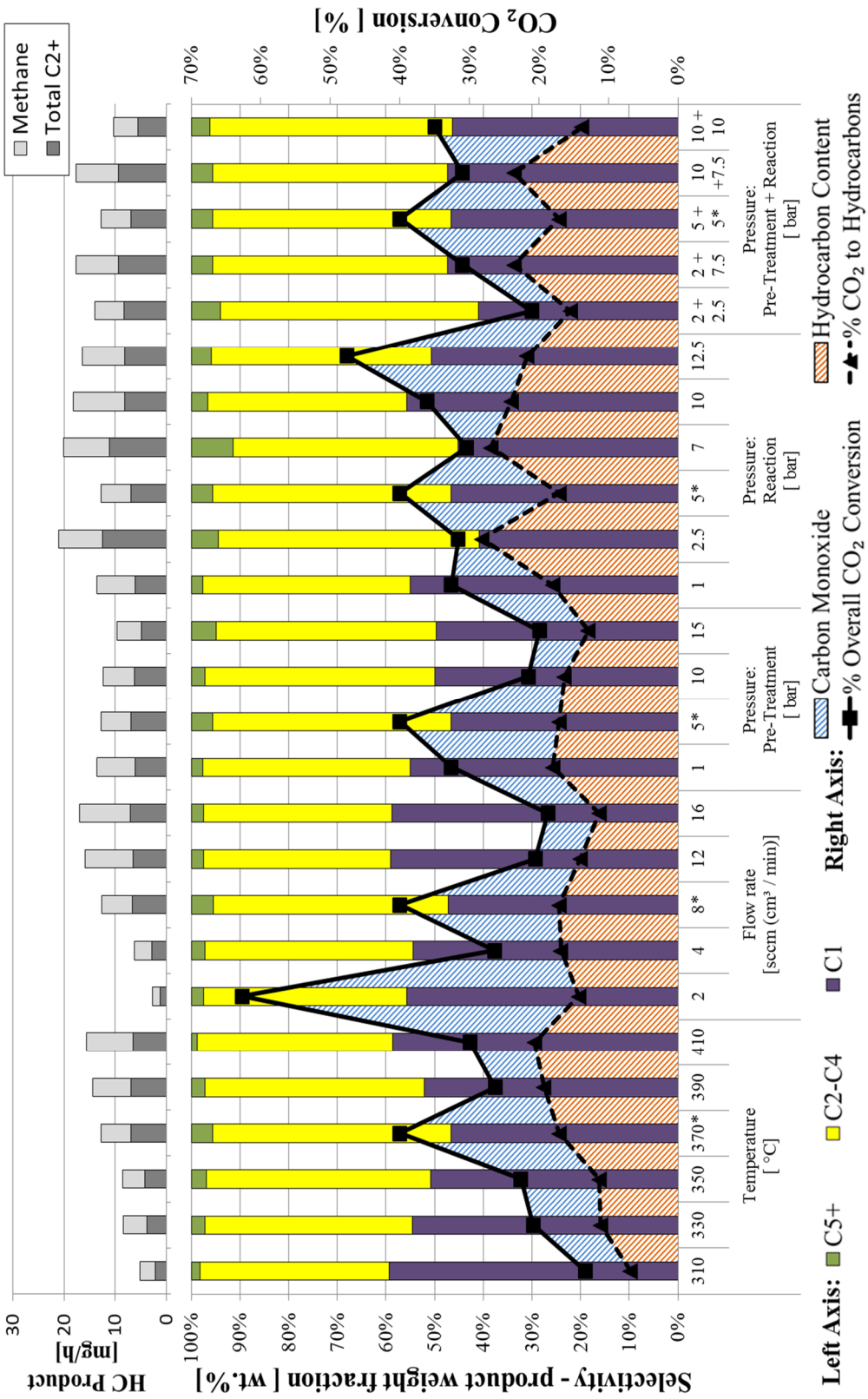


Figure 6-9 Performance across different reaction conditions for the MWCNTs with activated iron catalytic sites (Fe@CNT)

6.7.5.3 Offsetting impacts from the well of traditional hydrocarbons

Table 6-4 Identified formed products of the RWGS-FT process, and the representative datasets used.

Carbon atoms	HC products	Representative inventory data
C1	**methane**	**Natural gas for UK fields, transported to land via long-distance pipeline**
C2	**ethene, ethane**	**Ethene, from steam cracking, production mix, at plant, gaseous**
C3	**propene, propane**	**Propane/ butane, at refinery**
C4	**butene,** **iso-butane,** **n-butane**	**Butene, mixed, at plant** **Propane/ butane, at refinery** **Butanes from butenes, at plant**
C5	**pentane**	**Pentane, at plant**
C6	**hexane**	**Hexane, at plant**
C7	**heptane**	**Heptane, at plant**

Once specific hydrocarbon species, and their amounts, are known it was possible to allocate environmental impacts to them. Table 6-4 provides a breakdown of all the identified hydrocarbons (HC) formed using the RWGS-FT catalysts assessed in this chapter along with the representative life cycle inventory data used for the modelling of the HCs.

For the purposes of the modelled offset impacts, it was necessary to appreciate the process and supply chains which would be avoided by producing the HCs via the RWGS-FT process. This is termed hereafter as the 'HC Offset'. When choosing the datasets, care was taken to choose datasets providing:

- representation of the most common method likely to be used in the UK, and
- adequate cover life cycle stages which align with the modelled process, i.e. at the factory gate or ready for industrial uptake by other processes.

The HC datasets contained within Ecoinvent have been used which essentially detail the most common industrial synthesis routes of production. The GHG impacts per gram of these products is shown in Figure 6-10. These were verified using the supporting

Ecoinvent report literature (Sutter 2007), and Ullmann's encyclopaedia of industrial chemistry (Griesbaum *et al.* 2000).

Many datasets were present for methane, and the wide range in impacts attributable to these routes would cause significant effects in subsequent LCA work. Methane is the majority component of natural gas, and it is as natural gas in which methane is most used within the UK; for electricity generation, space heating and cooking. The representative mix chosen is the UK, long-distance pipeline dataset (Faist-Emmenegger *et al.* 2007), which represents the suitable gate impacts, from extraction to delivery on the UK mainland. Converting the volume of natural gas into the specific mass quantity of methane present, was made using the accompanying ecoinvent report (Faist-Emmenegger *et al.* 2007), and verified using the UK government conversion figures (MacLeay 2013).

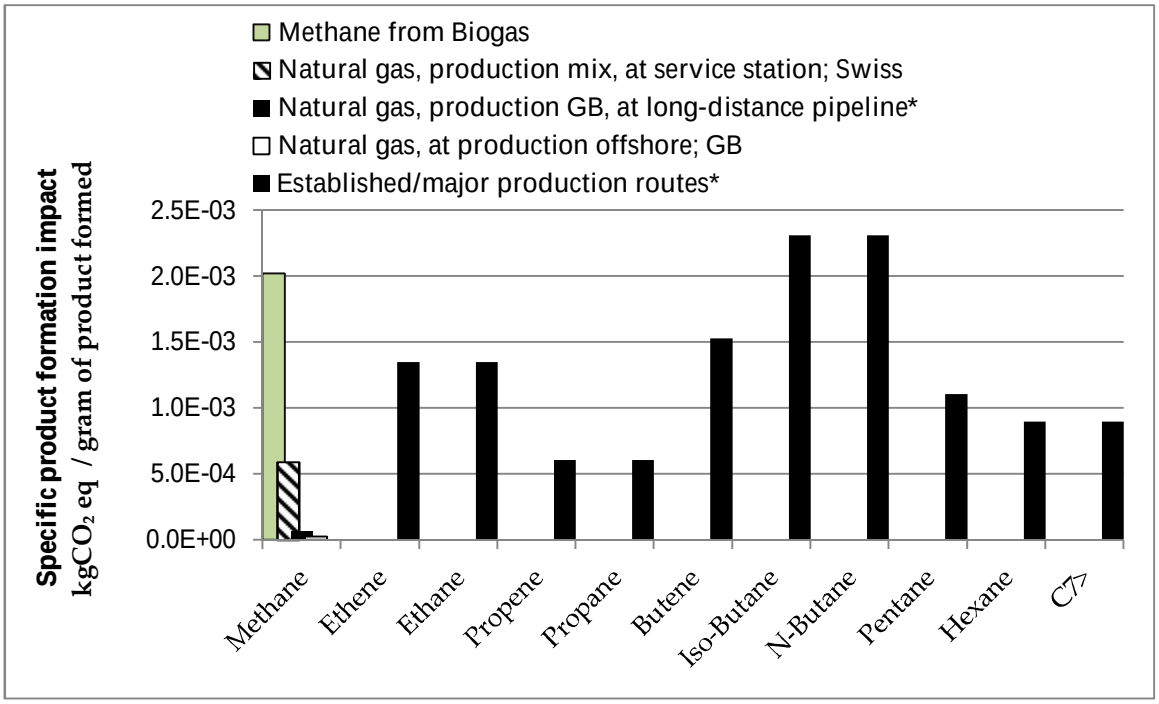


Figure 6-10 Equivalent hydrocarbon datasets, 1 gram of each respective species assessed across 18 midpoint environmental impact categories and cumulative energy demand. (Black bars represent datasets used in this LCA work).

Methane gas dataset is from an attributional study, however, the longer chained hydrocarbons based on the dataset for LCA work conducted on the extraction of crude oil, and subsequent allocation from this 'parent' LCI dataset occurs. The allocation of crude oil impacts occurs for their respective net heating value (Althaus *et al.* 2007). The allocation of process impacts to the formed products in this thesis has occurred via a proportional mass split of formed HCs. The adjustment of mass to lower heating values (to directly compare to Ecoinvent methodology) was not conducted since the discrepancy for the shorter-chained hydrocarbons assessed is ± 4% compared to using mass allocation alone; deemed close enough for comparison between datasets.

6.7.5.4 Equivalent life cycle stage assumption

It has been assumed that the obtained products from the tail-end of the RWGS-FT process are at an equivalent stage of the life cycle in comparison to the factory gate datasets within Ecoinvent. This has been justified since the product separation between C1 and C10 in a petrochemical distillation tower occurs at 350 °C (British Petroleum 2014) a lower temperature than the gases leaving the assessed RWGS-FT reactor.

The lightest hydrocarbon fractions require the least amount of post-processing before leaving the refinery (JACOBS Consultancy 2012). Furthermore, LCIA of light fraction oil refinery products were explored in Ecoinvent Database v2.2 (2010); e.g. naphtha, kerosene, butane and propane. It was found that the cross-category impact assessment results of these products are dominated by the extraction and delivery of the crude oil and the distillation tower heating. The footprint of plant infrastructure and other operational activities are found to be negligible. The majority of the refinery impacts are due to the heating of the crude oil in order to separate the products in the distillation tower, a stage not required due to the inherent heating of products in the RWGS-FT process. However, this is an assumption that will require revisiting should intensive separation routes be necessary.

6.7.6 *POTENTIAL FOR EXHAUST GAS RECYCLING*

An activity not occurring at the laboratory scale, however, undoubtedly one that would be attempted at larger process scales is the process of recycling exhaust gases. A large proportion of the feedstock gas remains unaltered after a single-pass over the catalyst

bed indicating obvious recovery would feed subsequent catalyst passes. Additionally carbon monoxide (CO), as shown in figures 6-7 and 6-8 makes up a significant part of the overall converted content. CO is an intermediary product in the RWGS-FT reaction, see equation 6-1, the product of the RWGS reaction before subsequent conversion to HCs in the final FT reaction step, equation 6-2. When stating any conditions considering exhaust gas recycling, the assumption taken is that gases not used to produce HCs will be re-introduced into the reaction chamber for subsequent reactions.

6.7.7 *MODELLING AN IDEAL CATALYST: ANDERSON-SCHULZ-FLORY DISTRIBUTION.*

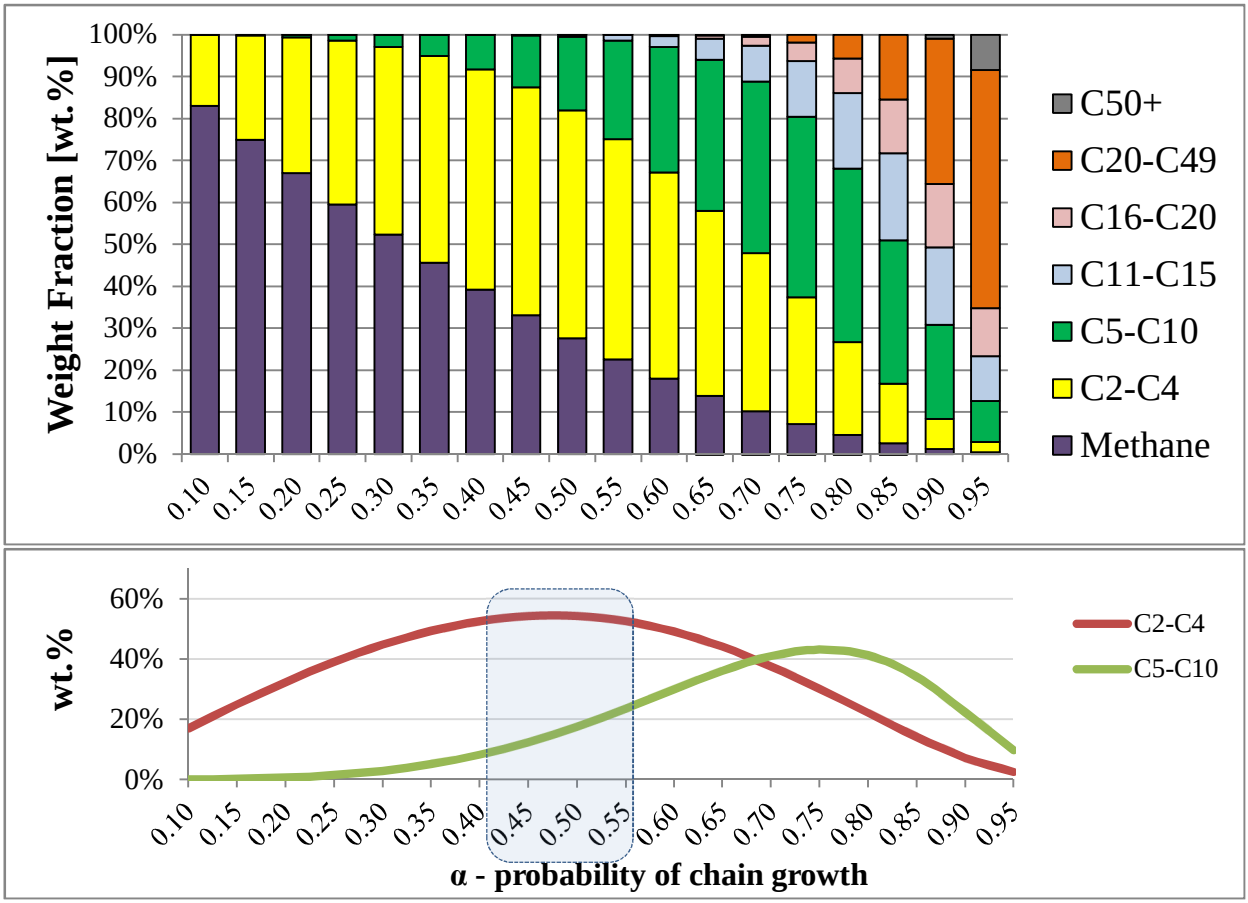


Figure 6-11 The weight fraction of Fischer-Tropsch products as per the Anderson-Schulz-Flory distribution equation.

Along with 'ideal band' in which catalysts should operate within to maximise production of highest value compounds (bottom).

The FT process does not produce one product in isolation, instead mixtures of hydrocarbons are formed, the selectivity i.e. proportion split between different hydrocarbons, is dependent on process conditions. The different formed product

distributions is shown across the catalysts at ambient pressure in figure 6-7, and for Fe@CNT across different reaction conditions of figure 6-8. The empirical values were empirically measured via gas sampling and analysis during the tested catalyst runs. However, the FT product distribution can also be theoretically approximated *via* the following, Anderson-Schulz-Flory (ASF), equation (Anderson *et al.* 1951):

Equation 6-12: ASF product distribution

$$\frac{W_n}{n} = (1-\alpha)^2 \alpha^{n-1}$$

Where, *n* refers to the number of carbon atoms present in any given hydrocarbon molecule, e.g. methane has 1, propane 3. *Wn* represents the weight fraction, or percentage by mass of total FT product formed, of a specific molecule with *n* number of carbons. The α term refers to the probability that the carbon chains formed in the process will tend to grow to be longer, i.e. contain more carbon atoms. Wn and n, are determined by α which in turn is specific to the chosen catalyst and the catalysis process reaction conditions. When $\alpha \approx 0$ only methane is created, as α increases towards 1 the weight fraction of longer chained molecules increases, until only thick waxes and tar products are obtained, as shown in Figure 6-11. Therefore, carbon chain lengths from C1, C2, C3 ….Cn, are dependent on catalyst material choice and reaction conditions.

For the purposes of the work at hand, and as per the demand profile of hydrocarbon products shown in Figure 6-1, the quantity of C2-C10 molecules are sought to be maximised. Whilst the production of methane, and – at the other end of the scale - waxes and longer chained hydrocarbons are to be minimised. Therefore, operating conditions of α near 0.5 is considered to be favourable condition; with approximately half of all products in lengths C2-C4, and a fifth C5-C10 hydrocarbons.

6.7.7.1 Defining the ideal catalyst performance

The ASF distribution closely fits what is seen in actual F-T processes (Anderson *et al.* 1951). Therefore, in addition to comparing tested catalysts *via* the conversion and selectivity recorded, an idealised case, for α =0.5, will be used. Furthermore, this case will consider 100% CO_2 conversion to hydrocarbons, thus presenting the best case environmental offset obtainable if an 'ideal' catalysis route could be achieved. Table 6-5

states the ideal mass quantities and split between different products. The ideal case denotes the highest 'ceiling' for a catalyst operating under the subjected CO_2 feed conditions, illustrative for establishing whether catalyst performance, or other life cycle impacts are the contributing limiting factors in reaching environmental sound process performance.

Table 6-5 Ideal weight distribution between formed products, and respective quantities formed per hour for; 100% conversion of 2 sccm CO_2 and 6 sccm H_2.

Carbon chain length	Produced Hydrocarbon Product	Weight distribution split [wt. %]	Amount of product [mg/hr]
C1	**Methane**	27.6%	20.8
C2	**Ethane/Ethene**	24.1%	16.5
C3	**Propane/Propene**	18.1%	12.4
C4	**Butane/Butene**	12.1%	8.3
C5	**Pentane/Pentene**	7.5%	5.2
C6	**Hexane**	4.5%	3.1
C7	**Heptane >**	6.0%	4.1
	Total	**100%**	**71.9**

6.7.8 *MODELLING ENERGY GENERATION FROM PROCESS HEAT*

Presently, the laboratory setup requires the input of heat energy in order for the process to occur. However, it is known for existing Fischer-Tropsch plants, that reactor cooling has been a primary design consideration since the first commercial plants of the 1920's (Davis 2005). The heat generation is understood once the thermodynamics of the process is considered. The overall enthalpy of reaction establishes the difference between the energy requirement for breaking reactant bonds, and the energy requirement for forming the bonds in the formed product.

Equation 6-13: Enthalpy of reaction

$$\Delta \boldsymbol{H} = \sum \Delta \boldsymbol{H}_{f_{products}} - \sum \Delta \boldsymbol{H}_{f_{reactants}}$$

$$\therefore \Delta H = energy\ for\ breaking\ bonds - energy\ for\ forming\ new\ bonds$$

Obtaining the differences between the enthalpies of the reactants and products of process determines whether or not a process is endothermic, requiring energy to proceed, or exothermic releasing energy as well as forming products. Referring back to the complete RWGS-FT reaction in Equation 6-3 (page 146), considering the simplified case of reactants and products at the same temperature and pressure, as is the case in the reaction chamber, Table 6-6 details the formation of FT products are always negative, i.e. exothermic in nature.

Table 6-6 Enthalpies of reaction for formation of different, carbon lengths C1-C7, Fischer Tropsch hydrocarbons

HC Molecule Formed	Reactants*			Products			∆H = H product - H reactants (kJ/mol)
	No. of CO_2	No. of H_2	∆H reactants (kJ/mol)	No. of HC	No. of H_2O	∆H products (kJ/mol)	
Methane	**1**	**4**	**- 394**	**1**	**2**	**- 559**	**- 165**
Ethane	**2**	**7**	**- 788**	**1**	**4**	**- 1,050**	**- 265**
Propane	**3**	**10**	**- 1,180**	**1**	**6**	**- 1,560**	**- 375**
Butane	**4**	**13**	**- 1,580**	**1**	**8**	**- 2,060**	**- 487**
Pentane	**5**	**16**	**- 1,970**	**1**	**10**	**- 2,570**	**- 598**
Hexane	**6**	**19**	**- 2,360**	**1**	**12**	**- 3,070**	**- 709**
Heptane	**7**	**22**	**- 2,760**	**1**	**14**	**- 3,610**	**- 855**

Chaumette *et al.* (1995) modelled the amount of obtainable heat available from the Fischer-Tropsch process, considering the product distribution from α, and the quantity of products being formed. In their work the model is founded on CO as the feedstock, this was adapted and expanded for the purposes of this thesis to cover CO_2. The resultant equation predicts the energy release per unit FT fuel produced.

Equation 6-14: The heat produced per kilogram of FT product (adapted from Chaumette *et al.*)

$$Q^{*}(\alpha) = \frac{-2.14 \propto^{2} + 15.13\alpha - 39.29}{16 - 2\alpha}$$

*non-SI units, whereby Q = kcal/kg. 1 joule = 0.239 calories.

The theoretically obtainable process heat from the FT process is shown for a gram of formed product in Figure 6-12. The amount of heat varies between 10 and 8 kJ dependent on process conditions, when taking $\alpha = 0.5$, the amount of energy is predicted to be 8.9 kJ per gram of product, or 2.47 kWh/kg. This value has been applied for all subsequent process assessments irrespective of final mix formed, since the error is within an acceptable level of approximately 10% when considering the minimum ($\alpha = 0$) and maximum (α=1) process variability; furthermore the actual catalyst performances sits much closer to the mean, α=0.5, value.

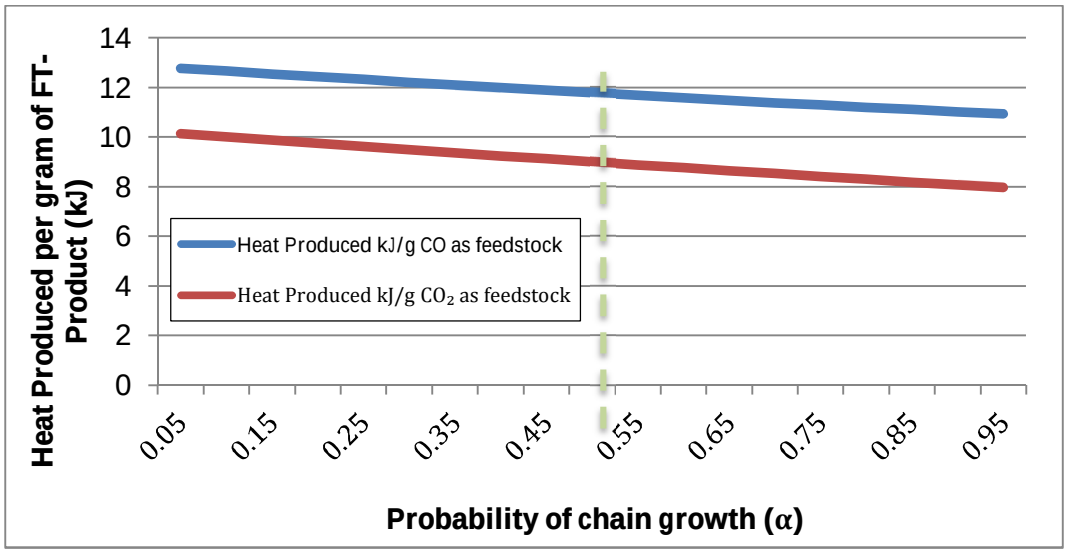


Figure 6-12 The heat release per gram of formed FT product, using eq. 11, value used in the LCA work refers to the α =0.5, which corresponds to 8.9 kJ.

In commercial FT plants, water/steam is used to prevent overheating and to moderate the temperature of the process (Jager and Espinoza 1995; Davis 2005), utilising this steam offers the potential for power generation. The concept of hydrocarbon and electricity co-production from the FT process has been of interest since the late 1970's (Steynberg and Nel 2004). The second law of thermodynamics governs the obtainable work from steam power generation of the process; the Carnot cycle provides a measure for the maximum amount of work recoverable by a heat engine operating between two heat reservoirs at different temperatures:

Equation 6-15: Carnot efficiency for heat engines

$$\eta = 1 - \frac{T_{ambient}}{T_H}$$

If the process were to run at the standard process conditions of 370 °C, in an ambient environment of 25 °C, then a maximum of ~54 % of the energy is obtainable. With the thermodynamic efficiency, extracting energy from steam, of turbines in a power plant in the range of 70 to 90%, the obtainable energy from the process is calculated to be closer to 48%. Considering the achievable efficiencies, and theoretical heat provision from equation 11, the produced electricity is approximated to be 1.19 kWh/kg of FT product.

This electricity generation approximation, in conjunction with the dataset produced for the UK electricity grid mix, allows the avoided emissions of generation *via* the recovery of waste heat to be calculated[6].

6.7.9 *MODELLING OF THE CATALYST LIFETIME*

The catalysts are modelled to have working lifetimes of 5000 hours, this is in-line with similar industrial processes (Lawrie Lloyd 2011). This length of sustained performance is an assumption for the catalysts at hand, since operation periods of ~ 48 hours are the longest runs to date. However, across this 48-hour period no measurable changes in performance were witnessed in terms of CO_2 conversion, or product selectivity. The current run times are agreeably many times less than the touted 5000 hour period, however, this is an anticipated performance target, indeed many Fischer-Tropsch catalysts have very long recorded service lives of 5 or so years (Davis 2007).

In later sections of this chapter the target lifetimes to meet environmental impact neutrality is presented; for different catalysts, reaction conditions, and scenarios. Thus providing design targets for catalyst / catalyst+infrastructure operational lifetimes required to realise environmentally beneficial returns.

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[6] ***Note****: the offset environmental impacts could also be modelled from the perspective of the heat generated being used directly, for instance by a subsequent industrial process. In this case there might be potential to further increase the benefit of this heat co-product, since there may be less thermodynamic losses as prevalent in conversion into electricity. Exploring the potential uses of waste heat in this manner is process dependent and considered outside of the scope of this work.*

6.7.10 *CATALYST EMBODIED IMPACTS*

The respective catalyst embodied impacts are outlined in the cradle-to-gate LCAs conducted in chapter 4 for the MWCNT based catalysts, and chapter 5 for the iron-palladium nanoparticles on silica. The mass quantities of catalysts used are assessed as they were tested within the reactor, and were dependent on the physical dimensions of the catalyst bed, see Table 6-1 (page 143). No attempt to normalise this data to a fixed quantity of catalyst has been conducted, since the process is scaled with the geometric conditions of the reactor and with the reaction conditions and flows, the catalytic performance is dependent on the function of the stated catalysts under these conditions. Furthermore, as covered in chapter 2, ENMs are more accurately assessed on the basis of their function rather than mass quantity amounts (Bauer *et al.* 2008).

Catalysts used are modelled for the worst and best environmental performance, as detailed in chapters 4 and5. The differences being:

- impacts of forming the catalysts as they presently stand in the lab,
- reduced impacts due to lean synthesis steps, use of renewable sources,
- modelling the recovery of precious metals from the palladium-based catalysts.

6.8 AMBIENT PRESSURE LCIA RESULTS FOR ALL TESTED RWGS-FT CATALYSTS

This section presents the environmental performance, of the suite of tested nanomaterials; both silica and carbon nanotube substrate, proven to be reverse water-gas shift – *coupled* – Fischer-Tropsch (RWGS-FT) capable catalysts. The assessed catalysis process is at an early developmental laboratory scale, founded on the inventory data outlined in section 6.5, and thus the life cycle impact assessment (LCIA) results are used for gaining insight of the system as it stands, and the provision of feedback towards a view of advancing the process to larger scales of development.

6.8.1 *LCIA RESULTS: LABORATORY PERFORMANCE CASE*

Figure 6-13 shows, the incurred and offset GHG values of each operating catalyst. It can be seen that the offset impacts are very small, almost untraceable, accounting between 0.01 and 0.13 % dependent on catalyst. It is for this reason that the values have been plotted on a logarithmic scale, for dissemination of discrete life cycle activity contributors.

Considering this, for all catalysts the avoided emissions from the produced hydrocarbons are in the region of 3 to 4 orders of magnitude, or factors of 1,000's and 10,000's away from offsetting the life cycle impacts of their formation. This is a very large deficit. The major prohibitive embodied impacts are due to the reaction energy, infrastructure and embodied catalyst impacts. The ideal catalyst is included for comparison (see background to ideal in section 6.7.7, page163), plotted on Figure 6-13, although a marked improvement in comparison to the tested catalysts, the boost in performance is insufficient, at 0.4%, to overcome the embodied impacts of running the RWGS-FT process.

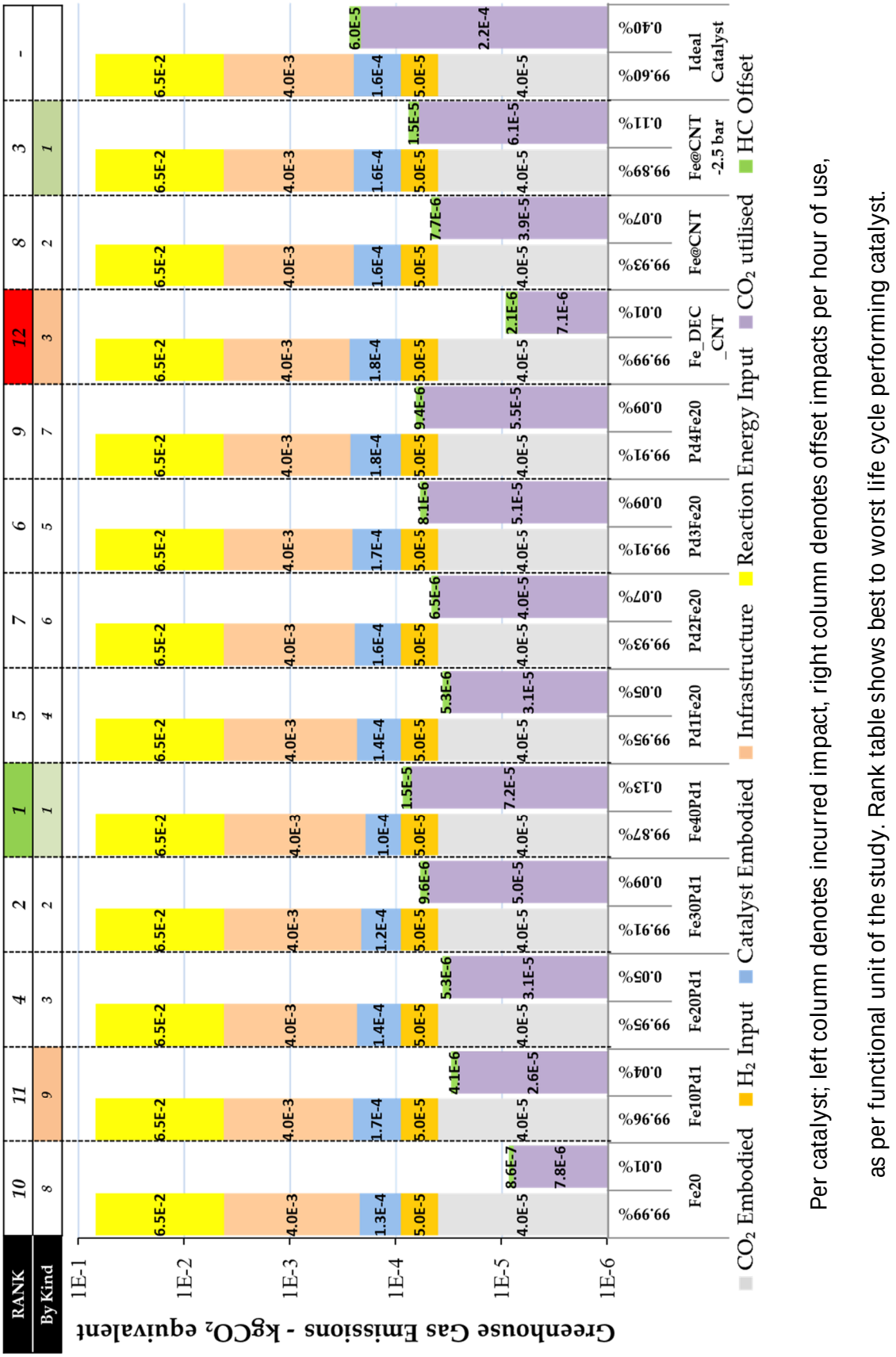
Catalyst selection is therefore not a limiting factor in achieving environmentally beneficial performance at these scales of operation, however, it is the catalytic performance, along with associated catalyst material embodied impacts, that differentiates the overall LCIA performance between catalysts. The rank order of best-to-worst, RWGS-FT catalysts, are presented above the bars of Figure 6-13; the ranking is

aggregate for all tested catalysts, and split by kind between the CNT and Fe-Pd-Silica catalysts.

Despite Fe20, being the lowest impact catalyst of all the silica based variants, see chapter 5, the short comings of if its in-use conversion mean that this catalyst's overall life cycle impact is the overall poorest performance. The best performing catalyst, Fe40Pd1, which in comparison to Fe20 offsets 10 times as much GHG emissions. However, even Fe40Pd1, only offsets 8.65×10^{-5} $kgCO_2$ eq, less even than the amount needed to offset the feedstock (CO_2 and H_2) has used. The modelled 'ideal catalyst', see section 6.7.7, performs approximately three times better than Fe40Pd1, offsetting 2.76×10^{-4} $kgCO_2$ eq. However, this carbon balance is still 99.60 : 0.40 % (incurred : offset). The high GHG deficit for the ideal case, is instructive in that even best possible catalytic performance is insufficient to get net beneficial GHG performance for the laboratory process setup.

6.8.1.1 Feedstock impacts

At the laboratory scales many incumbent impacts are preventing a favourable GHG performance, feedstock usage is one of these. The impacts of the captured CO2 and fossil fuel derived hydrogen outweight the total offset of all, but the ideal, catalysis processes. Indicative of the need to move towards renewable hydrogen utilisation for process feasibility, and of the recycling of all feedstocks to prevent losses.



Per catalyst; left column denotes incurred impact, right column denotes offset impacts per hour of use, as per functional unit of the study. Rank table shows best to worst life cycle performing catalyst.

Figure 6-13 The life cycle performance of all RWGS-FT catalysts at reaction conditions of: 2sccm of CO_2, 6sccm of H_2, 370 °C, and 1 bar reaction pressure.

6.8.1.2 Carbon Nanotube catalysts; related to Chapter 4

With an in-use life cycle activity measured, as detailed in Figure 6-13, it is possible to establish the relative impacts between the two MWCNT-based catalysts. Not only are the Fe@CNT catalysts less environmentally impactful in their synthesis, they are also better performing catalysts in comparison to Fe_Dec_CNT. The adoption of the novel embedded-activated catalyst (O'Byrne *et al.* 2013) over the traditional iron doped or decorated nanotubes provides a compound beneficial environmental affect. The use of the Fe@CNT catalyst from both a catalytic performance and LCA perspective is a 'win-win' choice over Fe_Dec_CNT.

6.8.1.3 Nanoparticle-silica catalysts; related to Chapter 5

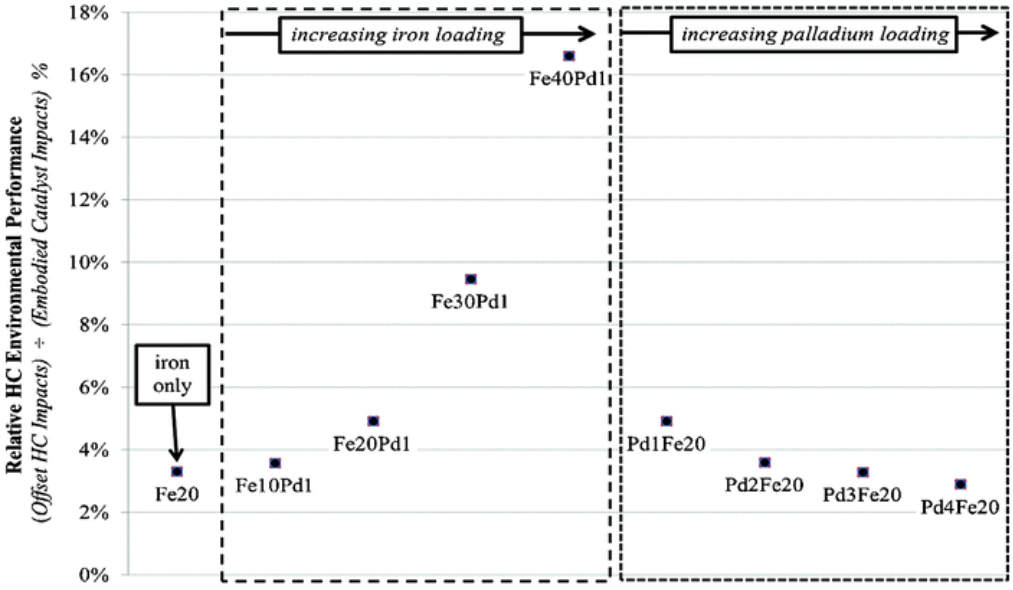


Figure 6-14 Comparing the incurred impacts through the formation of the catalysis vs. the offset impacts of producing HCs over 5000 h lifetime of the catalysts. Impacts are the summation of all ReCiPe midpoint category scores. (Griffiths *et al.* 2013b)

With a focus on comparing catalyst relative performance, Figure 6-14 relates the gate synthesis impacts of the different Fe-Pd catalysts, see chapter 5, against the offset impacts of forming HCs void of their traditional routes, see 6.7.5.3. The metric used for comparison is the sum of all ReCiPe midpoint impact categories to create an-unweighted single score, arguably a crude but indicative account of wider environmental considerations. As previously covered, at laboratory conditions, none of the iron:palladium catalysts have the potential to offset more GHG environmental impacts than they incur, with Fe40Pd1 managing to offset 16% of its synthesis impact.

Figure 6-14 negates the use of hydrogen, additional energy use, and reaction infrastructure effects on the environmental impacts. This focuses onto specific catalyst:product gains, for example, Fe40Pd1 and Fe20Pd2 display very similar catalytic performances, however, due to the incumbent environmental impacts of the additional palladium content Fe20Pd2 is performing far better in environmental terms.

Therefore, increasingly adding palladium does not return proportional benefits, even if higher CO2 conversions are seen. Indeed the worst performing Fe20 (iron only) catalyst has a comparable environmental relative performance to the higher loaded palladium catalysts.

6.8.2 *OVERALL FINDINGS FOR CATALYSTS AT AMBIENT PRESSURES AND LABORATORY SETUP*

All catalysts for the laboratory setups are performing unfavourably. For every catalyst tested the impacts associated with energy usage for the furnace heating, embodied materials of the associated laboratory infrastructure, and catalyst materials are each individually more damaging than any offset achievable through atmospheric CO_2 abatement and the avoided impacts of not sourcing the formed hydrocarbons from existing industrial sources. Since feedstock recycling is also not conducted at this scale then impacts of capturing the CO_2 and of producing the hydrogen are significant through gas wastage. The unreacted gases seen from Figure 6-8 are considerable, and thus if only a single pass is made across the catalyst bed only a fraction of the feedstock can ever be used.

6.9 HIGH PRESSURE CATALYST PERFORMANCE

In Figure 6-13 (page 172), amongst the list of tested catalysts (be they; iron-palladium-silica, and iron activated/decorated MWCNTs) is the result of the Fe@CNT catalyst operated at a reaction pressure of 2.5 bar, Fe@CNT-2.5bar, this condition represents the best environmentally performing catalyst with consideration of the catalyst conversion process and life cycle impacts of the different operating conditions. This section outlines the approach used to determine this finding.

The Fe@CNT catalyst, identified as the best performing MWCNT-based RWGS-FT catalyst in the previous section, was further tested in a high pressure laboratory reactor setup. Different process conditions, as shown in Figure 6-9 (page 159), resulted in differing catalytic performance for the Fe@CNT catalysts. Indeed, when compared to the 1 bar, or reference condition, higher CO_2 conversion and selectivity towards longer-chained hydrocarbons are witnessed for certain higher temperatures, flow rates and pressures. Gains in performance, however, need to be verified as net beneficial outcomes in the context of the whole life cycle, as illustrated in Figure 6-15. There are associated environmental penalties with increasing the intensity of a process, in a simplified case, the greater energy demand will lead to a proportional increase in GHG emissions. GHG impacts are modelled in isolation of the other impact categories, since favourable conditions in the context of CO_2 utilisation need to be achieved before wider environmental considerations occur; covered in later sections of this chapter.

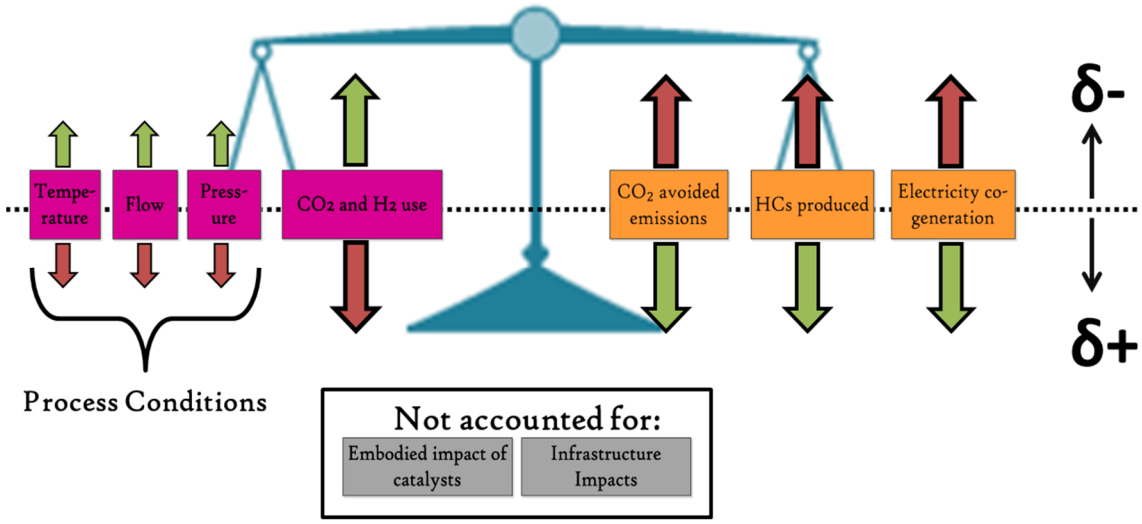


Figure 6-15 Balancing process performance gains versus associated penalties.

Comparative assessments in place of absolute life cycle impacts are measures, i.e. the δ values, to establish which condition is most environmentally optimal within the assessed reaction conditions. The delta, δ, values are measured from the 5 bar ***reference conditions***, which are:

- Temperature of 370 °C
- Feedstock flow of 8 cm3/min (sccm); 2 CO_2 + 6 H_2
- Gauge pressure of 5 bar

6.9.1 *RATIONALE*

Catalyst and infrastructure impacts remain constant across the tested reaction conditions, and thus have no effect on the δ values. The changing reaction conditions and resultant performance is measured:

6.9.1.1 Offsetting impacts

On the right side of the balance of Figure 6-15 are the elements affecting the offsets of the catalysis reaction. The net CO_2 offset emissions are related to the:

- quantity of CO_2 locked away in the product and thus immobilised from the atmosphere; conversions given in Figure 6-9 (page 159)
- equivalent mix of hydrocarbons being offset; combining selectivity towards products Figure 6-9 (page 159), with the impacts of forming these *via* traditional routes 6.7.5.3 (page 160).
- Exploitation of process heat; to power a turbine generating electricity to displace the UK grid mix impacts for the equivalent delivered electricity 6.7.8 (page 165).

6.9.1.2 Incurring Impacts

The operation of the process, and changing of reaction parameters affects the incurred burdens; left side of Figure 6-15. Changing temperature, flowrates, and pressures are result in changing energetic requirements. Modelled *via* the provision of energy being provided by the UK electricity generation mix, the net carbon balance is obtained. The hydrogen and CO_2 feedstock is constant, but will be used in differenting amounts for the changing flowrate conditions.

The outcome is to establish which condition is optimal in terms of limiting the environmental burden and maximising the environmental offset of the overall catalytic process.

6.9.2 *CO_2 OFFSET FOR DIFFERENT REACTION CONDITIONS*

Table 6-7–Changes to offset GHG impacts, measured relative to reference condition.

~Increasing rank number denotes more offset impacts~

		CO_2 Locked-in	Offset HC	Offset Grid	∑ Offset	
δ values - kg CO_2 eq.		3.7E-05	8.4E-06	8.2E-06	5.3E-05	
		± δ	± δ	± δ	± δ	Rank
Temperature [°C]	310	-2.2E-05	-5.8E-06	-4.9E-06	-3.3E-05	21
	330	-1.3E-05	-3.7E-06	-2.8E-06	-1.9E-05	19
	350	-1.2E-05	-3.2E-06	-2.7E-06	-1.8E-05	18
	370*				0	12
	390	4.6E-06	1.9E-08	1.1E-06	5.7E-06	10
	410	7.6E-06	-4.8E-07	1.8E-06	8.9E-06	9
Flow rate [sccm]	2	-2.9E-05	-7.0E-06	-6.5E-06	-4.3E-05	22
	4	-1.9E-05	-4.9E-06	-4.2E-06	-2.8E-05	20
	8*				0	12
	12	8.7E-06	-2.8E-07	1.9E-06	1.0E-05	8
	16	1.2E-05	2.6E-07	2.6E-06	1.5E-05	6
Pressure: Reaction [bar]	1	2.0E-06	-1.0E-06	5.0E-07	1.4E-06	11
	2.5	2.4E-05	6.5E-06	5.3E-06	3.6E-05	1
	5*				0	12
	7	2.1E-05	5.3E-06	4.7E-06	3.1E-05	2
	10	1.5E-05	2.0E-06	3.5E-06	2.0E-05	3
	12.5	9.9E-06	1.5E-06	2.3E-06	1.4E-05	7
Pressure: Pre-Treat + Reaction [bar]	2 + 2.5	-3.5E-06	1.7E-06	7.9E-07	-1.1E-06	16
	2 + 7.5	1.4E-05	2.9E-06	3.1E-06	2.0E-05	4
	5 + 5*				0	12
	10 +7.5	1.4E-05	2.9E-06	3.1E-06	2.0E-05	5
	10 + 10	-7.1E-06	-1.6E-06	-1.6E-06	-1.0E-05	17

The process gains, or the enhanced GHG offsets for the tested reaction conditions are presented in Table 6-7. When accounting for the GHG impacts the unit used is $kgCO_2$ equivalent emissions, i.e. covering the spectrum of GHG's normalised to the radiative forcing effects of CO_2. The total offset is the summation of the CO_2 locked inside the

formed hydrocarbons, the offset or avoided emissions through not sourcing the hydrocarbons from fossil fuel reserves, and finally in the case of considering reaction heat release, the co-generation of electricity thus proportionally offsetting an equivalent UK electricity grid impacts.

When considering the performances relative to the 370 °C / 8sccm / 5 bar reaction condition, i.e. the datum in which the reaction δ's are taken from, the reference condition sits amongst the middle in terms of overall ranked offsets. Higher temperatures, flow rates, and all changing pressures yield higher GHG offsets. The offset is directly linked to the amount of CO_2 converted and the selectivity towards specific and traditionally more impactful hydrocarbons. The 2.5bar reaction pressure performs the most favourably, offsetting almost twice the reference case offset; an additional 3.6×10^{-5} $kgCO_2$ eq/hour, on top of the datum's 5.3×10^{-5} $kgCO_2$ eq/hour.

The worst performance when considering the reaction products in isolation are for the lower flow rates of 2 and 4 sccm, and the lower, <370 °C, reaction temperatures. Reduced flowrate has the direct effect of less CO_2 being available to be react, limiting the overall performance. The catalysts are also clearly performing at a lower rate for the cooler reaction temperatures.

6.9.3 *CO_2 INCURRED FOR DIFFERENT REACTION CONDITIONS*

The process for calculating the energy and thus GHG environmental impact for different reaction conditions is calculated through a combination of direct measurements and theoretical calculations. Section 6.7 of this chapter details the manner in which inventory energy consumption for different conditions has been calculated. The resultant GHG impacts are presented within this chapter, based on the theoretical energy intensity values.

In the case of the efforts in varying reaction temperatures both direct and theoretical values are presented in Table 6-8. The net effect between theoretical and laboratory measured temperature impacts has a significant bearing on the overall incurred impact; appreciated by an increase by three orders of magnitude. The differences between actual and theoretical measurements differ by a factor of between ~900 and 2000 depending on the temperature setpoint; indicating the thermal inefficiencies of the actual process. The

large differences between actual and theoretical temperature energy are reflected in Table 6-8, whereby temperature ceases to be the omni-dominant process impact for the theoretical case. As a result of the high impacts attributed to the furnace heating, in the actual measured case the best and worst overall performing catalysts are those with the lowest and highest reaction temperatures respectively.

Table 6-8 – Direct measured GHG impacts incurred for different reaction conditions. Measured temperature energy (top) and theoretical minimum energy (bottom) ~Increasing rank denotes increasing incurred impacts~

		Lab Temp.	Theory Temp.	Flowrate	Pressure	Feedstock	Laboratory ∑ Incurred		Theoretical ∑ Incurred	
δ values - kg CO_2 eq. /hr		5.9E-02	3.3E-05	3.0E-17	1.7E-05	1.8E-05	5.9E-02		6.9E-05	
		± δ	± δ	± δ	± δ	± δ	± δ	Rank	± δ	Rank
Temp [°C]	310	-1.6E-02	-5.7E-06			-1.1E-05	-1.6E-02	1	-1.7E-05	3
	330	-1.1E-02	-3.8E-06			-6.4E-06	-1.1E-02	2	-1.0E-05	5
	350	-5.4E-03	-1.9E-06			-6.2E-06	-5.4E-03	3	-8.0E-06	7
	370*						0	8	0	8
	390	1.1E-02	1.9E-06			2.3E-06	1.1E-02	21	4.2E-06	13
	410	2.2E-02	3.8E-06			3.8E-06	2.2E-02	22	7.9E-06	16
Flow rate [sccm]	2		-2.5E-05	-2.9E-17	-1.3E-05	-1.4E-05	-2.8E-05	4	-5.2E-05	1
	4		-1.7E-05	-2.6E-17	-8.7E-06	-9.3E-06	-1.8E-05	5	-3.5E-05	2
	8*						0	8	0.0E+00	8
	12		1.7E-05	7.1E-17	8.7E-06	4.3E-06	1.3E-05	16	3.0E-05	21
	16		3.3E-05	2.1E-16	1.7E-05	5.9E-06	2.3E-05	20	5.6E-05	22
Pressure: Reaction [bar]	1				-1.7E-05	9.8E-07	-1.6E-05	6	-1.6E-05	4
	2.5				-7.7E-06	1.2E-05	4.2E-06	12	4.2E-06	12
	5*						0	8	0.0E+00	8
	7				4.0E-06	1.0E-05	1.4E-05	17	1.4E-05	18
	10				8.6E-06	7.4E-06	1.6E-05	18	1.6E-05	19
	12.5				1.2E-05	4.9E-06	1.7E-05	19	1.7E-05	20
Pressure: Pre-Trea + Reaction [bar]	2 + 2.5				-7.7E-06	-1.7E-06	-9.4E-06	7	-9.4E-06	6
	2 + 7.5				4.9E-06		1.2E-05	14	4.9E-06	14
	5 + 5*				0.0E+00	0.0E+00	0	8	0.0E+00	8
	10 +7.5				4.9E-06	6.9E-06	1.2E-05	15	1.2E-05	17
	10 + 10				8.6E-06	-3.5E-06	5.0E-06	13	5.0E-06	15

Although the pressures and flow rate impacts are calculated in all cases *via* theoretical means, the inefficiencies of compression technologies are included in an attempt to bring the values in-line with more realistic expectations. Achieving higher efficiencies for pressures and flows are easier, since leakages and resistances to flow are small in comparison to heat transfer losses in actual working practice. Thus the energy penalty

will always be lower for achieving the desired flow rates and pressures for this system in comparison to the temperature conditions.

Measuring the different flow rates is two-part; the effort required to achieve the desired flow, modelled as pressure differences across the reactor, and the embodied environmental impacts of the reduced/increased feedstocks.

In the case of theoretically calculated impacts, increasing the flow rate from 2 to 16 sccm sees the largest overall effect on impacts. Since increased flow requires increased energy to meet the: temperature rise, flow rate, and pressure conditions, and more embodied impact from the consumption of more H_2 and CO_2 feedstock. Conversely lower flowrates have the lowest incurred GHG impact. After flow rate conditions are considered, the next most influential impact is the pressure requirement. With 1 bar condition performing best, the elevated 10 bar and 12.5 bar performing the worst.

6.9.4 *NET LIFE CYCLE IMPACTS OF DIFFERENT REACTION CONDITIONS*

Table 6-9 Resultant GHG impact

		Laboratory	Theoretical
Net GHG impact [kg CO_2 eq. / hour]		**5.9E-02**	**1.5E-05**
		± δ	± δ
Temperature [°C]	**310**	-1.6E-02	1.6E-05
	330	-1.1E-02	9.3E-06
	350	-5.4E-03	1.0E-05
	370*		
	390	1.1E-02	-1.5E-06
	410	2.2E-02	-1.4E-06
Flow rate [sccm]	**2**	1.5E-05	-9.7E-06
	4	9.8E-06	-6.7E-06
	8*		
	12	2.7E-06	1.9E-05
	16	8.5E-06	4.2E-05
Pressure: Reaction [bar]	**1**	-1.8E-05	-1.8E-05
	2.5	-3.2E-05	-3.2E-05
	5*		
	7	-1.7E-05	-1.7E-05
	10	-4.4E-06	-4.4E-06
	12.5	2.9E-06	2.9E-06
Pressure: Pre-Trea + Reaction [bar]	**2 + 2.5**	-8.4E-06	-8.4E-06
	2 + 7.5	-8.2E-06	-1.5E-05
	5 + 5*		
	10 +7.5	-8.2E-06	-8.2E-06
	10 + 10	1.5E-05	1.5E-05

6.9.4.1 Actual temperature impact

Table 6-9 details the net overall GHG impact for the different reaction conditions. When considering the actual laboratory measured process it can be appreciated that the temperature requirement of the reaction is the overriding factor. Confirmation of this is witnessed as the three conditions with a net beneficial impact in comparisons to the reference (370 °C / 8sccm / 5 bar) reaction condition, are for the occasions in which the furnace is operating at the three lower temperatures 310, 330 and 350 °C. Furthermore, the two worst process conditions are for the elevated 390 and 410 °C.

If this process were to be developed from a laboratory to a larger scale setup then it is clear that addressing the heat requirement would be necessary for the process to be in anyway *via*ble. However, a fundamental difference would also be seen as the scale extends towards larger capacity reaction infrastructure. Indeed, as previously reported, larger scale Fischer-Tropsch reactors require cooling to address overheating issues due to the exothermic reaction. This exothermic nature is not fully witnessed, nor admittedly measured, for the particular process under investigation. Although it is assumed that due to the relatively small throughput of reactants and transient nature of the gases within the reaction chamber, any temperature increase is carried through into the exiting exhaust gases.

If one were to consider a larger scale process, the heat requirement is replaced with heat provision (Steynberg and Nel 2004). In this process, there are no environmental burdens associated with the differing reaction temperatures; instead the process heat is utilised for power generation, offsetting the current UK electricity grid mix provides a beneficial GHG contribution to the process.

6.9.4.2 Theoretical temperature impacts

Due to the system boundaries under consideration, the extra infrastructure and values for obtainable electricity energy are not available to consider and are therefore out of scope for a fair comparative LCA to occur. Therefore, stays with the current setup, however presents the theoretical minimum or ‘target’ process GHG impact for the provision of the different reaction temperatures across the different temperature ranges.

For the theoretical process resultant GHG impacts, it can be seen that 11 reaction conditions perform better than the reference datum condition.

The higher temperatures give marginal gains for the theoretical case, varying pre-treatment with reaction temperatures has also a notable effect. However, of more significance two reaction conditions, 1 and 2.5 bar pressures, have negative overall GHG values.

Understandably, these processes cannot be stated as GHG / carbon neutral since the reaction infrastructure and catalyst embodied impacts are excluded from the assessment. Instead it presents the operational envelope in which the remaining life cycle activities must fit within if this goal is to be pursued.

Three processes perform better than the reference condition but do not offer a net negative potential. The 7 bar reaction condition is marginally better than the reference condition. The lower impacts witnessed by the 2sccm and 4sccm process conditions can be considered tri*via*l results. The relative CO_2 conversion of 2sccm and 4sccm are indeed greater than the reference condition. However, without considering the inherent process impacts, which are equal across all conditions, increasingly decreasing flowrates will result in overall reduction in yield and thus potential environmental offset achievable from a potential operating plant – which has 'invested' environmental impact which requires nullifying in order to be a *via*ble process. However, it does illustrate the positive effects of maximising the reaction performance to minimise the wastage of impactful H_2 and CO_2 feedstocks.

6.9.4.3 Best operating condition

For the Fe@CNT catalyst, however, it was found that the 2.5 bar reaction condition was not only better from a catalytic, but also an LCA perspective. For the Fe@CNT catalyst tested, the 2.5 bar reaction pressure is not only more efficient than the reference high pressure condition, but also better than the ambient reaction setup. It is for this reason that the 2.5 bar reaction pressure is modelled in conjunction with the other CNT and Fe-PD catalysts in the following scenario analysis of the operating RWGS-FT process.

6.10 SCENARIO ANALYSIS: MOVING AWAY FROM THE LABORATORY SETUP

This section, *via* the means of a sensitivity analysis of the dominant process activities, suggests a series of implementable life cycle changes for the benefit of improving the current laboratory setup. Appreciating that the laboratory process for all tested catalysts is many orders of magnitude from being a *via*ble CO_2 utilising process as shown in Figure 6-13 section 0, a sensitivity analysis on the most dominant life cycle impacts was undertaken to investigate the potential feasibility of the RWGS-FT processes under investigation.

The results of Figure 6-16 are the hypothesised improvements in which the laboratory impacts might reach; a best case scenario at this scale, with consideration of further process improvements that might be achieved when moving towards larger scale roll-out. The discrete life cycle incurred impacts are minimised, and the offsets maximised by a series of conservative changes to the LCA model of the process.

6.10.1 *PROCESS ENHANCEMENTS*

The adopted 'lean' laboratory setup and other process enhancement measures include:

- The catalyst embodied impacts are those presented as the 'best cases' synthesis gate impacts, from chapters 4 and 5. Lean synthesis, renewable resource, end-of-life precious material recovery are all being considered.
- The reaction energy is supplied from renewable source of wind power generation, emitting 10 g CO_2eq/kWh, compared to the modelled UK grid mix of 540 g CO_2eq / kWh.
- The supply of hydrogen is *via* renewable electrical electrolysis of seawater.
- Enhanced operational efficiency, represented by laboratory equipment being used to full capacity, and no ramp-up, ramp-down or idle periods.
- Catalyst furnace a third of the size of reference laboratory, since this would still maintain required reaction temperatures across the bed. Mass flow controller

allocation is based on max deliverable flow, rather than assigning one meter per reactor; i.e. 8 out of the maximum 450 sccm obtainable.

- A feedstock gas recycling loop is hypothesised, whereby the impacts attributable to the use of the H_2 and CO_2 reactant gases are significantly minimised, since unreacted gas is considered to be available for subsequent re-use and catalyst bed passes.

6.10.2 *IMPROVED SCENARIO FINDINGS*

The lean process model shown in Figure 6-16, can be considered a significant improvement in environmental terms over the current baseline (shown in Figure 6-13). However, the performance is appreciably still orders of magnitude away from GHG, or 'carbon', neutrality.

For the laboratory baseline model, the impacts are almost indistinguishable between CNT and the FePd-Silica formed catalysts. However, with reference to the improved and lowered gate impacts of the respective materials (see Chapters 4 and 5). The embodied impacts of the Fe20 (i.e. no palladium) and the MWCNT catalysts (also no palladium content) are the lowest, in the context of the overall suite of catalysts assessed. With reference to overall ranking shown in Figure 6-16, the best (Fe40Pd1) and worst (Fe_DEC_CNT) in-use catalytic performances of candidate iron-palladium catalysts remain unchanged. However, subtelties appear within the rankings due to the changing impacts for the best case modelled catalyst gate impacts.

The resultant incurred:offset percentile figures are improved with Fe40Pd1 93.6 : 6.4 %, and the best performing carbon nanotube catalyst, Fe@CNT 94.3 : 5.7 %.

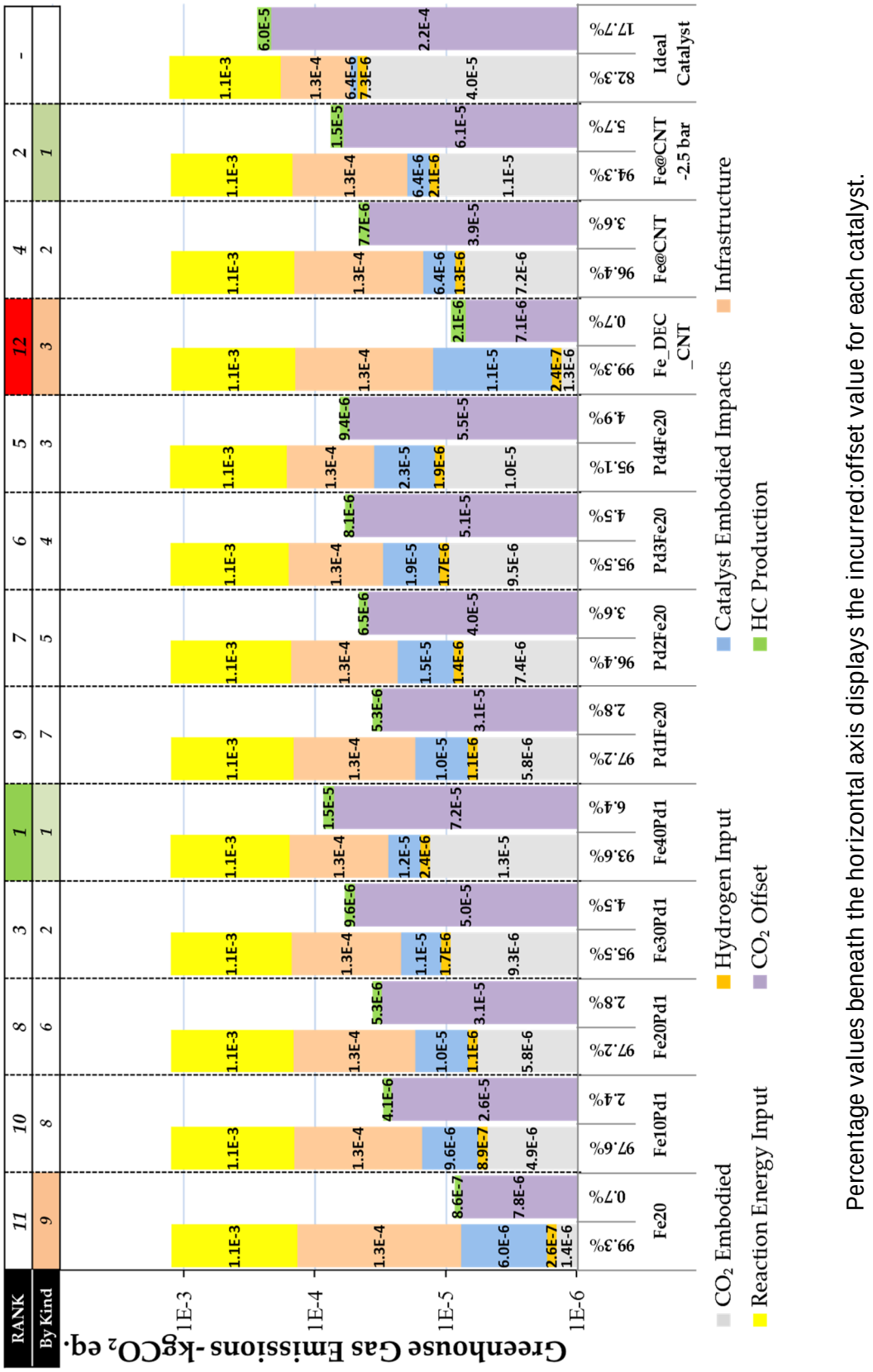


Figure 6-16 Improved RWGS-FT process. Within the confines of the current laboratory setup, however, incorporating best case life cycle inputs

6.10.3 *PROCESS ENERGY FLUX*

In alignment with the methodological approach detailed in section 6.7.8, it is possible to consider the demand for energy being eliminated, and the potential for energy recovery from the process to occur, shown in Figure 6-17. This has an overwhelming bearing on the environmental performance of the RWGS-FT, bringing the process closer to being a feasible alternative to traditional hydrocarbon synthesis pathways. For this condition, heat generated by the reaction, is deemed sufficient for feedstock heating, i.e. an autothermal reaction, in addition to potential heat recovery for electricity generation. Electricity offset is shown as red bars in Figure 6-17. However, despite modelling this favourable switching energy flux, only an 'ideal' RWGS-FT catalyst would return a net-benefit GHG performance.

The rank order of the catalysts at the heat recovery model do not change, as they remain constant and in alignment with the previous section.

6.10.4 *FURTHER INFRASTRUCTURE IMPROVEMENTS STILL NEEDED*

The embodied impacts of the operational infrastructure are a final hurdle in achieving GHG life cycle offsets. Infrastructure impacts can be considered an order of magnitude more impactful in comparison to other incurred life impacts, thus they must be reduced. Table 6-10 details the target amount in which infrastructure impacts must not exceed, in comparison to present (leanly used) laboratory equipment model, to meet or exceed GHG neutral impacts.

The significance of meeting this target would result in the processes being beneficial from the perspective of CO_2 use as a feedstock and the formation of HCs from the RWGS-FT route over traditional petrochemical routes. Impacts below zero, i.e. negative, indicate that infrastructure change alone is not sufficient for process to reach GHG neutrality, and figures >100% (only present for modelled 'ideal' catalyst) state that a process is already achieving GHG negative life cycle impacts for the current 'lean' laboratory setup.

Table 6-10 Target infrastructure impacts, relative to lean setup, to reach GHG neutrality for a 5000 hour catalyst process.

	Fe20	Fe10Pd1	Fe20Pd1	Fe30Pd1	Fe40Pd1	Pd1Fe20	Pd2Fe20	Pd3Fe20	Pd4Fe20	Fe_DEC_CNT	Fe@CNT	Fe@CNT-2.5bar	*Ideal Catalyst*
%	2	16	20	37	57	20	24	30	31	-1	32	54	208

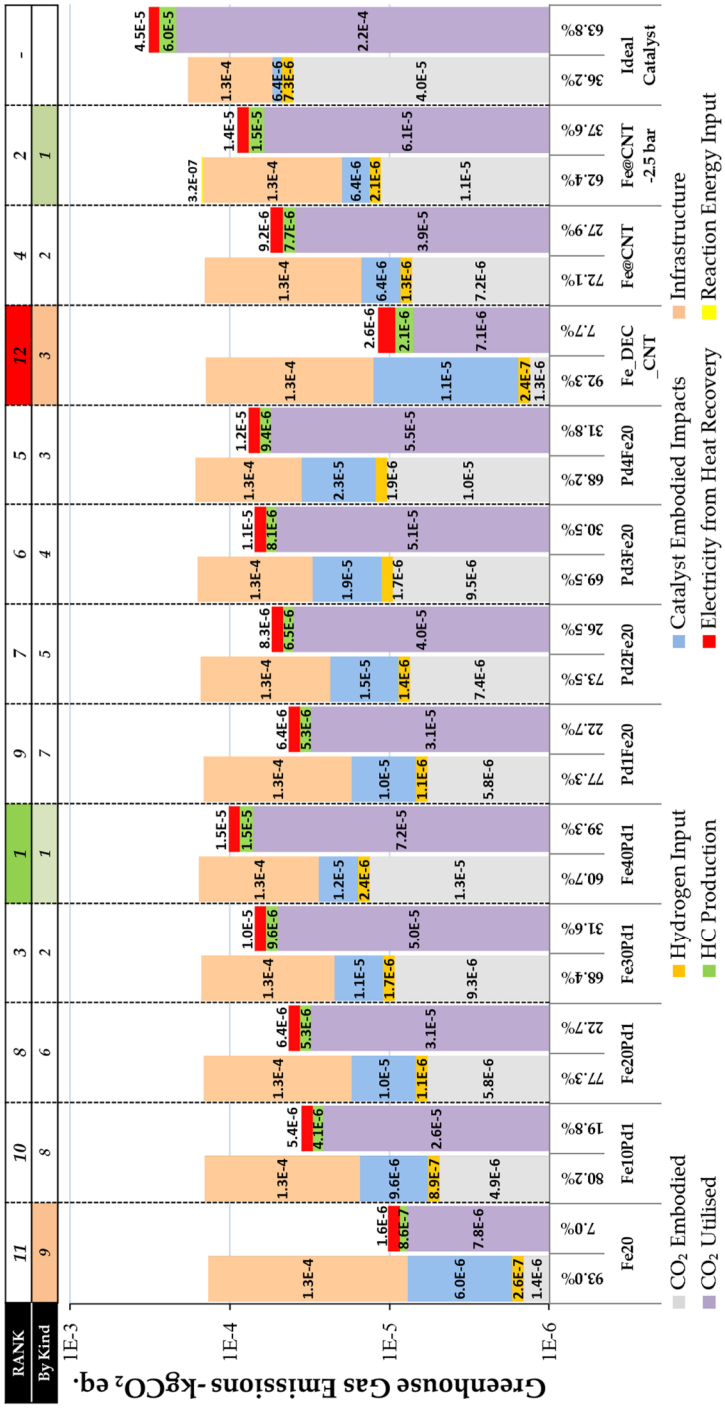


Figure 6-17 Best case RWGS-FT, considering process heat extraction.

6.10.5 *SENSITIVITY TO SELECTIVITY AND MODELLING DATASETS USED FOR THE PRODUCED HYDROCARBONS*

Table 6-11 The quantity of HCs produced by the different catalysts, and the respective GHG emissions being offset.

	Total FT Fuel Mass			Offset GHG		
	miligrams	% of ideal	Rank	$kgCO_2$ eq	% of ideal	Rank
Fe20	**2.5**	***4%***	**12**	**8.6E-07**	***1%***	**12**
Fe10Pd1	**8.5**	***12%***	**10**	**4.1E-06**	***7%***	**10**
Fe20Pd1	**10.0**	***14%***	**8**	**5.3E-06**	***9%***	**8**
Fe30Pd1	**16.2**	***23%***	**5**	**9.6E-06**	***16%***	**3**
Fe40Pd1	**23.3**	***33%***	1	**1.5E-05**	***25%***	**2**
Pd1Fe20	**10.0**	***14%***	**9**	**5.3E-06**	***9%***	**9**
Pd2Fe20	**12.9**	***18%***	**7**	**6.5E-06**	***11%***	**7**
Pd3Fe20	**16.6**	***24%***	**4**	**8.1E-06**	***13%***	**5**
Pd4Fe20	**18.0**	***26%***	**3**	**9.4E-06**	***16%***	**4**
Fe_DEC_CNT	**4.0**	***6%***	**11**	**2.1E-06**	***3%***	**11**
Fe@CNT	**14.3**	***20%***	**6**	**7.7E-06**	***13%***	**6**
Fe@CNT @2.5 bar	**21.1**	***30%***	**2**	**1.5E-05**	***25%***	1
Ideal' FT Catalyst	**70.4**	***100%***		**6.0E-05**	***100%***	

There is a great deal of sensitivity regarding the mix of hydrocarbons formed, and the models used to represent these. The product yield and respective offset GHG emissions of the different catalysts are shown in Table 6-11. In terms of mass quantity, Fe40Pd1 is producing the highest overall, producing a third of what an 'ideal catalyst' would achieve for the same quantity of gaseous feedstock. This reinforces that conversion to hydrocarbons alone is not necessarily an accurate account of the environmental performance of the catalyst.

The selectivity of the catalyst is an important factor on the overall offset impact. For example, the Fe@CNT catalyst operating at 2.5 bar stands second in terms of quantity of HC yield, however produces the largest Greenhouse Gas (GHG) offset. Whereas the best catalysts are producing a third of the total mass an ideal catalyst, they are only offsetting a quarter of the ideal's potential GHG offset.

For traditional production pathways methane, in comparison to the other longer chained hydrocarbons, has a considerably lower life cycle impact. Representative life cycle dataset for methane is natural gas extracted from a UK offshore facility and piped to the mainland, whereas other hydrocarbons are distillates of a petrochemical refinery. Thus meaning, having a bias, or selectivity, towards longer-chained hydrocarbons but

with a lower yield, can result in greater offsets than catalysts with higher yields but of the less environmentally beneficial product.

For instance a catalyst able to convert 100 % of the CO_2 to methane, would produce approximately 75 mg of fuel, this would place it above all other tested catalysts in terms of yield. Yet, the respective offset GHG would only come to 5×10^{-6} $kgCO_2eq$, or 8% of the ideal, placing it amongst the worst of the catalysts under investigation. Thus conversion and selectivity of HC products are important in the development of catalysts.

The LCA outcomes would strongly enforce the drive to produce catalysts with a reduced tendency towards methane production. This statement, however, is dependent on the chosen source of methane to be offset. From the LCA datasets used (Ecoinvent Database v2.2 2010) methane from natural gas routes is between 25 and 90 times less impactful than the routes for other C2-C7 hydrocarbons being produced. Widening this assessment to other alternatives non-fossil fuels, bio-methane was approximately found (Ecoinvent Database v2.2 2010) to be 80 times more impactful than natural gas (see Figure 6-10, page 161), in this there would be at the very least little penalty and some cases a positive benefit for the production of methane over all other hydrocarbons. Such an emphasis from one life cycle element within the whole assessed system, demonstrates the power of the LCA methodology to glean findings of this nature. However, it is also an example of where the system boundaries and modelling assumptions made are of paramount importance in the reporting of LCA work to stakeholders.

From previous work however it is known that the second best catalysts, Fe40Pd1 from Table 6-11 is the overall best life cycle catalyst. This is due to the additional offsets achieved by more converted mass of fuel resulting in more CO2 being locked into the products, and indeed more potential extractable electricity from the reaction heats. LCA is allowing the subtleties and importance of the co-factors and co-products to be appreciated.

6.11 FULLER LIFE CYCLE IMPACT CONSIDERATION

LCA allows environmental trade-offs to be considered, across the wider range of environmental impacts in addition to carbon footprinting alone. In addition to GHG, the other 18 assessed impacts are considered. For the best performing iron-palladium (Fe40Pd1), and carbon nanotube (Fe@CNT) catalysts, the operational impacts are shown in Figure 6-18 and Figure 6-19 respectively. These figures include the whole operational consideration of the process under lean conditions, with the most favourable life cycle inputs in terms of catalyst impacts, recycling of input gases, renewable utilisation.

As covered in section 6.10.4 (page 186), Fe40Pd1 and Fe@CNT can both potentially achieve GHG neutrality for 5000 hour catalyst lifetimes, 30 year infrastructure. This is achieved when operational infrastructure impacts are lowered to at least 57 %, for Fe40Pd1, and more for Fe@CNT to 32% Fe@CNT, see Table 6-10.

Figure 6-18 and Figure 6-19 demonstrate this neutrality by balancing the incurred : offset for the climate change category, i.e. split 50% either side of x-axis. Noteworthy here is that CO_2 locked-into the products is only influencing climate change (GHG) impacts, the remaining categories rely solely on hydrocarbon offset and the production of process heat. For the majority of categories the offsets fall short of the embodied impacts of the operating process.

Few impact categories in addition to GHG neutrality, achieve environmentally favourable returns with offsets exceeding the proportional share by -50% or more. In terms of overall proportional impacts, both Fe40Pd1 and Fe@CNT catalysts yield similar full impact assessment result profiles with GHG amongst the few impacts being offset; along with natural land transformation, fossil depletion, and cumulative energy demand. The offsets can be appreciated to be interlinked with regard to the consumption of non-renewable fossil fuel reserves. Where as the production methods for traditional HCs are lower in comparison to the RWGS-FT route, thus not offering meaningful offsets.

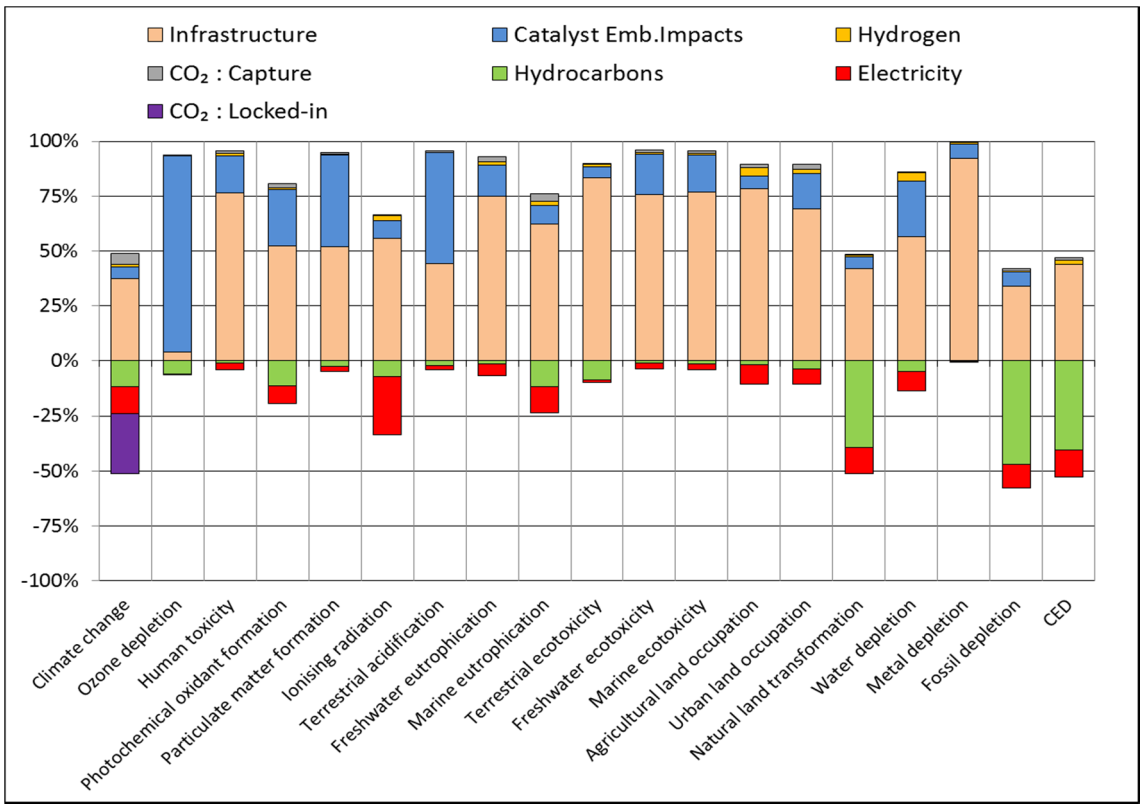


Figure 6-18 The 1 hour operational impact of catalyst Fe40Pd1. Best case; 57% infrastructure, renewable electricity, and renewable hydrogen.

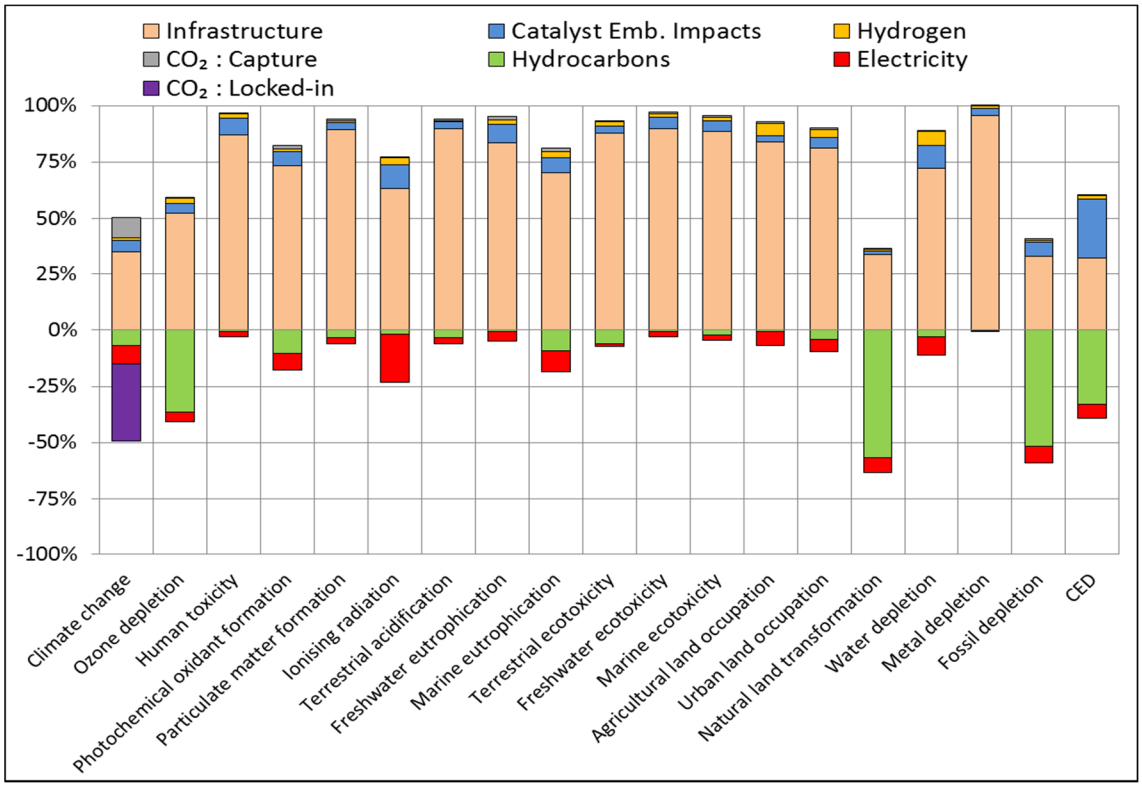


Figure 6-19 The 1 hour operational impact of catalyst Fe@CNT. Best case; 32% infrastructure, renewable electricity, and renewable hydrogen.

The reduced catalytic performance of Fe@CNT in comparison to Fe40Pd1 result in proportionally less hydrocarbon offsets and generated electricity, however, the lower impact Fe@CNT catalyst lowers the incumbent burdens. Common for both processes, and all tested RWGS-FT catalyst routes investigate, the process infrastructure and catalyst embodied impact are the most dominant; addressing these impacts are necessary in order for the wider environmental categories to be neutralised. Infrastructure impacts require further investigation, since it can be assumed for the present that catalyst impacts are already indicative of their lowest likely impacts, presented as the best cases:

- Fe@CNT; see lean catalyst synthesis of 4.5, page 97, and
- Fe40Pd; see section 5.7.4, page 133.

Fe@CNT very nearly offsets ozone depleting potential impact, however, the catalyst embodied impact of Fe40Pd1, and indeed all of the synthesised iron:palladium catalysts of Chapter 5, are high due to the same root-cause, being the laboratory infrastructure used. Specifically fluorine based seals present in the vacuum pump used during the evaporation stage of the catalyst synthesis, see section 5.6.1, page 121

This has demonstrated that GHG assessment alone is not sufficient when wishing to account for the full life cycle impact of the process. Despite hypothetical lean process, and further infrastructure reduction, changes to the LCA model the majority of impacts assessed the RWGS-FT process are significantly more impactful.

6.11.1 *EXPLORING INFRASTRUCTURE IMPACTS, AND POTENTIAL FOR IMPROVEMENT*

As shown previously in Figure 6-18 and Figure 6-19, the majority of life cycle impacts of the processes arise from the embodied environmental impact of the laboratory equipment used, displayed as ‘Infrastructure’. These infrastructure impacts are percentages of a lean setup to meet GHG break-even conditions, which in turn is an improvement on the currently witnessed laboratory process. i.e. best exploitation of the laboratory equipment. Establishing the source, and potential mitigation of this impact is thus an avenue to be explored.

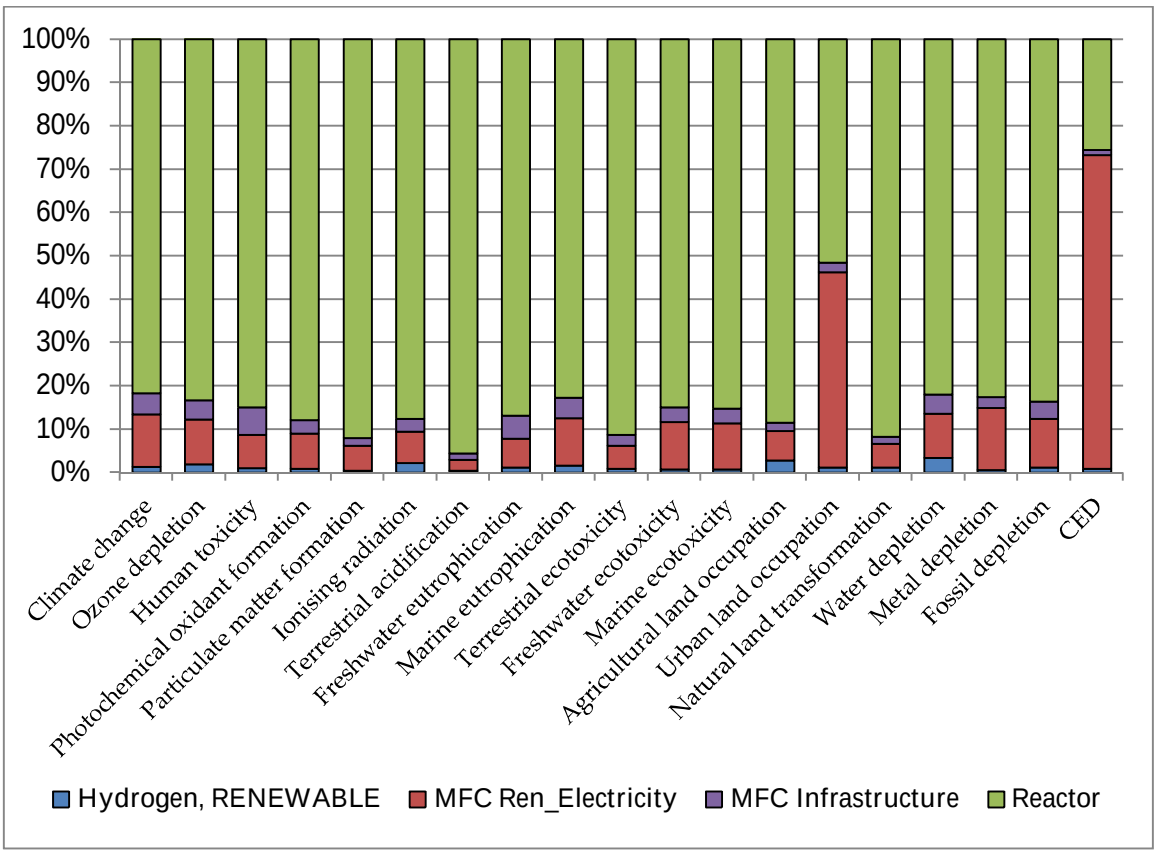


Figure 6-20 Characterised impact breakdown for the modelled infrastructure

The life cycle impacts of the infrastructure of the running catalytic process are shown in Figure 6-20. The reactor construction and embodied material impacts are the source, > 85 %, for all impact categories. Indeed, if the impacts of the reactor infrastructure were to be negated, then all bar one (ozone depletion for Fe40Pd1) of the impacts for the catalytic processes would be favourable, in Figure 6-18 and Figure 6-19.

Infrastructure impact reduction has to this point in the chapter been treated with blanket reductions in order to meet environmentally beneficial operational targets. However, considering a more explorative approach of investigating the componentry parts of the infrastructure device it is possible to establish the potential impact mitigation *via* constituent part recovery and recycling.

Considering an end-of-life (E-O-L) take back of equipment and the recovery of major constituent parts is outlined in chapter 4, since the reactor is identical to that assessed in MWCNT growth activities. Thus meaning, for the EOL conditions reported later in the chapter, the impacts of metals and glass constituents are largely recovered. However, further reduction would potentially be achievable, specifically focused on:

- **The negation of nickel impacts;** appreciably a major impact across the majority of impacts, especially those highlighted in Figure 6-18 and Figure 6-19 as presently being prohibitively environmentally impactful. Nickel is used for the heating elements within the reactor. These elements are necessary at laboratory scale, however, at larger scales the exothermic nature of the reaction would result in no heat provision being required.

- **Review of controller infrastructure for different scale processes;** the furnace controller is responsible for maintaining the reactor at a constant specified temperature. This control system will always be required, however, the impacts of its use are not likely to be always as prominent with a larger scale. Meaning, a larger reactor would not require a proportionally larger controller, indeed apart from perhaps more thermocouple / temperature measuring devices being present the integrated circuit and method of control are likely to remain nominally similar irrespective of the physical geometry of the reactor.

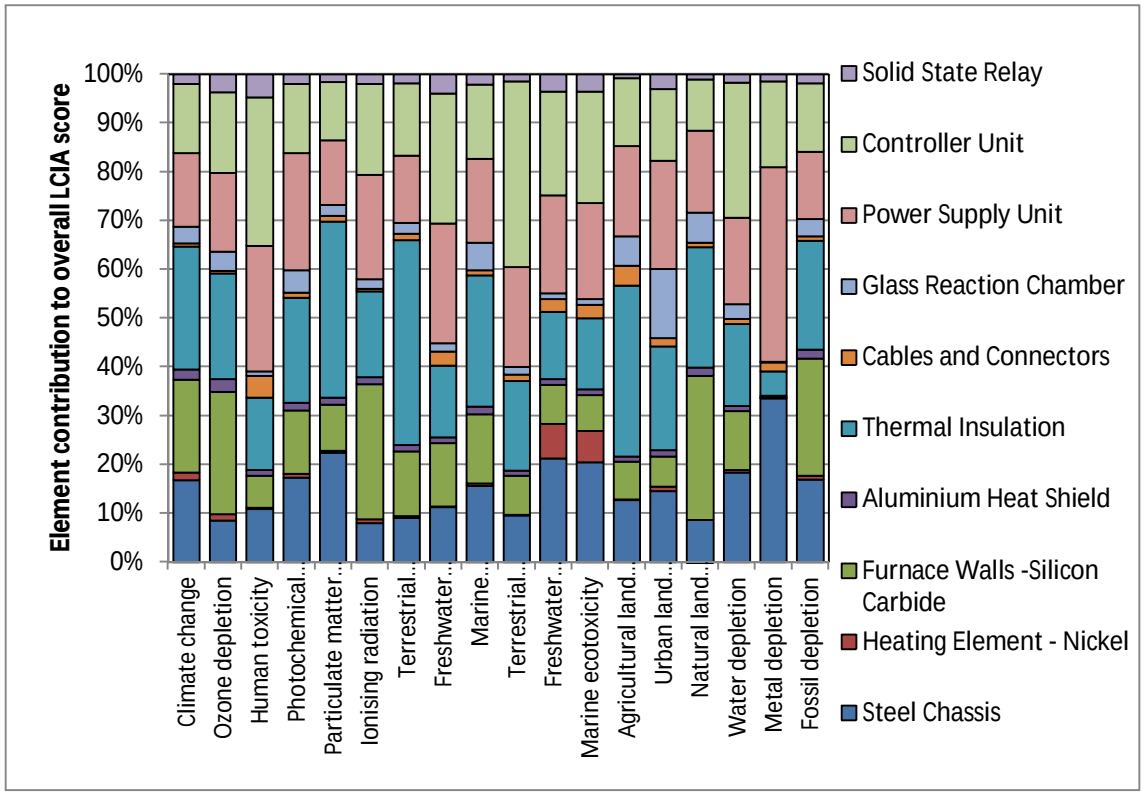


Figure 6-21 Percentage breakdown of the contribution of the different elemental parts of the tube reactor (same as shown in Chapter 4).

6.12 SETTING OPERATIONAL TARGETS

The background methodology for this section is stated in Chapter 3, section 3.8.4 (page 66). Relating the incurred versus offset impacts of the operating process; seen as the left and right columns of: Figure 6-13, Figure 6-16, and Figure 6-17.

Different to previous sections, this analysis ignores predefined infrastructure serviceable lifetimes (~30 years) and 5000 hour catalyst operation periods, in order to identify the lifetimes that must be exceeded to achieve favourable environmental returns. The uncoupling of catalyst and infrastructure from predetermined expected operational lifetimes brings forward new insight into the operational performance of the catalysts, offering the technical feasibility of sustained operation of the processes to be considered.

In order for the RWGS-FT catalysts to offer a potential net environmental benefit two conditions must be met:

- Condition 1: The in-reaction (dynamic) offset must outweigh the incurred impact.
- Condition 2: The catalyst (and associated operational infrastructure) must operate long enough at the net-negative impact rate in order to offset the initial embodied (static) impacts.

When both of these conditions are satisfied a break-even point, or minimum serviceable lifetime, for the catalyst (C), and catalyst with infrastructure (C+I) can be obtained. That is the period of operation that must be exceeded before beneficial environmental impacts are witnessed, in comparison to traditional production routes of HC production; see section 6.7.5, page 157.

Table 6-12 Modelling assumptions for the different Case scenarios assessed

<table>
<tr><th></th><th>Furnace Energy</th><th>Infrastructure</th><th>Catalyst</th><th>Feedstock</th></tr>
<tr><td>Case 1</td><td rowspan="3">No heat input. Process considered to be operating in a thermally self-sustaining manner.</td><td>As in laboratory</td><td>As in laboratory. As presented in chapters 4 and 5 respectively.</td><td>As in laboratory. Single pass of CO_2 and H_2 reactant gases.</td></tr>
<tr><td>Case 2</td><td rowspan="3">As in laboratory. Additional end-of-life recovery of bulk materials; metals, glass</td><td>Enhanced material handling and energy usage; ‘lean’ representation of laboratory. E-O-L recovery of 70% of catalyst metal constituent.</td><td rowspan="4">Feedstock gas recycling. Whereby the unreacted CO_2, and intermediate CO product are fed back for additional passes over the catalyst bed, so that all feedstock is eventually converted into hydrocarbons.</td></tr>
<tr><td>Case 3</td><td rowspan="2">Same as Case 2 and 3, but with renewable wind power used for electricity source during catalysts synthesis steps.</td></tr>
<tr><td>Case 4</td><td rowspan="2">Energy extraction for electricity co-generation</td></tr>
<tr><td>Case 5</td><td>10 % of laboratory. With same E-O-L as Cases 2 to 3.</td></tr>
</table>

It has been established that, as the laboratory process presently stands, there is a requirement for process energy in order for the reaction to occur. This impact is prohibitively large, resulting in condition 1 never being met. This stands true if energy is sourced from the UK national grid, or from a renewable wind generator.

Therefore, larger process scales for the RWGS-FT reaction is required to realise the exothermic nature of the CO_2 –to-hydrocarbon reaction for the benefit of sustaining the reaction autothermally; thus negating the need for energy consumption. Indeed, full exploitation of process heat could provide the potential for co-generation, a beneficial contributor in meeting condition 1.

In order to fully explore the potential environmental feasibility of the assessed RWGS-FT catalysis routes, a series of case scenarios are hypothesised, the background assumptions and modelling of the cases are detailed in Table 6-12.

6.12.1 *RESULTS OF TARGET SETTINGS*

The different modelled cases are tabulated for the four candidate materials:

- Fe20; Table 6-14
- Fe40Pd1; Table 6-15
- Fe@CNT; Table 6-16
- Fe@CNT for 2.5 bar reaction pressures; Table 6-17

The feasibility is expressed as the time period before break-even points in the respective environmental impact categories are achieved, for easier visualisation of this the cells are colour coded, see Table 6-13.

Table 6-13 Key for coloured cells within this section

Cell colour	Time period before break-even
	< 1 year
	Between 1 and 10
	Between 10 and 50
	> 50 years
	Never breaks even

Table 6-14 Environmental pay back periods (in years) for Fe20

Fe20	Case 1		Case 2		Case 3		Case 4		Case 5	
	C	C + I	C	C + I	C	C + I	C	C + I	C	C + I
Climate change			11.3	1.0E+3	0.5	806	0.4	616	0.4	62
Ozone depletion	2.2E+3	2.0E+4	13	2.0E+3	9.4	2.1E+3	7.6	1.7E+3	7.6	181
Human toxicity										
Photochemical oxidant form					50.1	8.5E+4	1.7	2.8E+3	1.7	285
Particulate matter formation							4.4	9.3E+3	4.4	934
Ionising radiation							0.3	3.0E+3	0.3	304
Terrestrial acidification							3.6	6.1E+3	3.6	613
Freshwater eutrophication										
Marine eutrophication							2.5	3.9E+3	2.5	390
Terrestrial ecotoxicity			73	1.5E+4	13.0	4.0E+4	4.9	1.5E+4	4.9	1.5E+3
Freshwater ecotoxicity										
Marine ecotoxicity							9.3	1.2E+4	9.3	1.2E+3
Agricultural land occupation							7.5E+3	4.6E+7	7.5E+3	4.6E+6
Urban land occupation							22.0	8.7E+3	22.0	891
Natural land transformation	6.7	1.4E+3	3.6	562	0.1	566	0.1	4.9E+2	0.1	49
Water depletion							8.8	9.6E+3	8.8	970
Metal depletion			102	6.4E+4						
Fossil depletion			10.6	1.2E+3	0.2	618	0.2	514	0.2	52
Cumulative Energy Demand			15.0	1.7E+3	3.1	886	2.4	688	2.4	71
Non-Renewable CED			14.6	1.6E+3	0.2	808	0.2	635	0.2	64

Table 6-15 Environmental pay back periods for Fe40Pd1

Fe40Pd1	Case 1		Case 2		Case 3		Case 4		Case 5	
	C	C + I	C	C + I	C	C + I	C	C + I	C	C + I
Climate change			0.94	115	0.11	94	0.08	67	0.08	6.8
Ozone depletion	22.06	281	0.80	153	0.56	160	0.47	134	0.47	13.8
Human toxicity							4.96	1.4E+3	4.96	141
Photochemical oxidant form			17.86	1.4E+3	2.75	374	1.13	154	1.13	16.4
Particulate matter formation			95	4.5E+3	28.57	1.6E+3	7.69	423	7.69	49.2
Ionising radiation			34.40	4.6E+3	1.2E+3	2.4E+6	0.12	240	0.12	24.1
Terrestrial acidification			93.0	2.1E+3	3.9E+1	991	11.28	286	11.28	38.7
Freshwater eutrophication							2.30	1.3E+3	2.30	127
Marine eutrophication			25.07	3.4E+3	1.27	924	0.28	204	0.28	20.6
Terrestrial ecotoxicity	3.9	3.1E+3	1.99	515	0.44	603	0.34	469	0.34	47.3
Freshwater ecotoxicity							5.94	1.1E+3	5.94	120
Marine ecotoxicity			21.49	2.8E+3			2.87	593	2.87	62
Agricultural land occupation							0.53	1.5E+3	0.53	150
Urban land occupation			9.37	1.6E+3			1.14	399	1.14	41.0
Natural land transformation	0.4	118	0.32	69	0.03	69	0.03	57	0.03	5.7
Water depletion			9.00	1.3E+3			0.73	349	0.73	35.5
Metal depletion	108	3.1E+5	6.86	1.3E+3						
Fossil depletion			0.61	95	0.04	63	0.03	51	0.03	5.1
Cumulative Energy Demand			0.85	130	0.25	88	0.19	66	0.19	6.8
Non-Renewable CED			0.82	124	0.05	81	0.04	62	0.04	6.2

Table 6-16 Environmental pay back periods for Fe@CNT

Fe@CNT	Case 1		Case 2		Case 3		Case 4		Case 5	
	C	C + I	C	C + I	C	C + I	C	C + I	C	C + I
Climate change			1.5	172	0.1	136	0.09	111	0.1	11.2
Ozone depletion	1.6	493	0.7	276	0.1	294	0.12	259	0.12	26.0
Human toxicity										
Photochemical oxidant form					1.0	1.1E+3	0.40	418	0.40	42.2
Particulate matter formation					10.1	1.4E+4	1.00	1.4E+3	1.00	136
Ionising radiation			191	2.2E+4			0.37	690	0.37	69
Terrestrial acidification					5.1	5.9E+3	0.76	869	0.76	88
Freshwater eutrophication										
Marine eutrophication					10.1	1.1E+4	0.60	648	0.60	65
Terrestrial ecotoxicity	10.4	14,007	2.1	1.1E+3	0.7	1.5E+3	0.58	1.2E+3	0.58	120
Freshwater ecotoxicity										
Marine ecotoxicity							5.30	3.3E+3	5.30	337
Agricultural land occupation										
Urban land occupation			45.8	7.8E+3			1.75	2.0E+3	1.75	201
Natural land transformation	1.3	192	0.6	109	0.0	110	0.03	98	0.03	9.8
Water depletion			70	1.1E+4			2.23	1.8E+3	2.23	186
Metal depletion			14.6	4.3E+3						
Fossil depletion			1.5	195	0.1	106	0.09	93	0.09	9.3
Cumulative Energy Demand			2.1	269	0.7	151	0.60	125	0.60	13.0
Non-Renewable CED			2.1	256	0.1	139	0.10	115	0.10	11.6

Table 6-17 Environmental pay back periods for Fe@CNT-2.5bar

Fe@CNT -2.5 bar	Case 1		Case 2		Case 3		Case 4		Case 5	
	C	C + I	C	C + I	C	C + I	C	C + I	C	C + I
Climate change	1.8	221	0.9	104	0.1	85	0.06	70	0.06	7.1
Ozone depletion	0.8	253	0.4	149	0.1	157	0.06	142	0.06	14.2
Human toxicity										
Photochemical oxidant form			23.4	2.9E+3	0.4	387	0.20	211	0.20	21.3
Particulate matter formation			26.0	6.6E+3	1.2	1.6E+3	0.46	620	0.46	62
Ionising radiation			37.0	4.3E+3			0.23	433	0.23	43.5
Terrestrial acidification			14.2	2.5E+3	0.8	956	0.35	401	0.35	40.5
Freshwater eutrophication										
Marine eutrophication			131	1.6E+4	1.0	1.0E+3	0.30	323	0.30	32.6
Terrestrial ecotoxicity	1.9	2.5E+3	0.8	454	0.3	533	0.23	467	0.23	46.9
Freshwater ecotoxicity										
Marine ecotoxicity							2.72	1.7E+3	2.72	173
Agricultural land occupation							5.05	2.0E+4	5.05	2.0E+3
Urban land occupation			11.6	2.0E+3			0.82	931	0.82	94
Natural land transformation	0.9	135	0.5	78	0.0	79	0.02	70	0.02	7.0
Water depletion			8.0	1.2E+3			0.80	658	0.80	66
Metal depletion	55	3.0E+5	4.7	1.4E+3						
Fossil depletion			1.0	122	0.1	69	0.06	61	0.06	6.1
Cumulative Energy Demand			1.3	166	0.5	98	0.39	81	0.39	8.5
Non-Renewable CED			1.3	158	0.1	90	0.06	75	0.06	7.6

For Case 1, only the Fe@CNT_2.5bar catalyst has the potential to offer a net negative GHG balance, this comes from a net offset impact being achieved (see Best operating condition', (page 182)). Albeit the time periods for this payback are very large for the catalyst and infrastructure at over 200 years operation, but as stand-alone catalyst

material it would payback its embodied carbon within 1.8 years. The better catalytic-conversion performing of Fe40Pd1 is not able to meet the condition 1 criteria, due to the high embodied impacts of the palladium metal constituents. For much of Case 1 across the assessed catalysts and conditions the majority of the 19 chosen environmental impact categories are not offset. Adoption of case 2, analogous to improved scenario of section 6.15, offer all catalysts the potential to overcome GHG in addition to a majority of the other environmental impacts. However, unfeasibly large payback periods remain in place for the majority of impacts.

Modelling heat recovery for electricity generation, as is Case 4, has a marked although for the most part not significant implication on payback periods when compared to case 3 which is identical however not considering heat recovery. Technology developers would require further work to determine if the investment in energy recovery would be a sound decision to make given the marginal gains witnessed.

The 'best case scenario', Case 5, as expected yields the most promising results.

- Fe40Pd1, GHG payback in ~ 6.5 years overall, majority of other within one to two decades of operation.

- Fe@CNT-2.5bar; GHG in ~7 years, other impacts on the whole requiring up to four decades of operation.

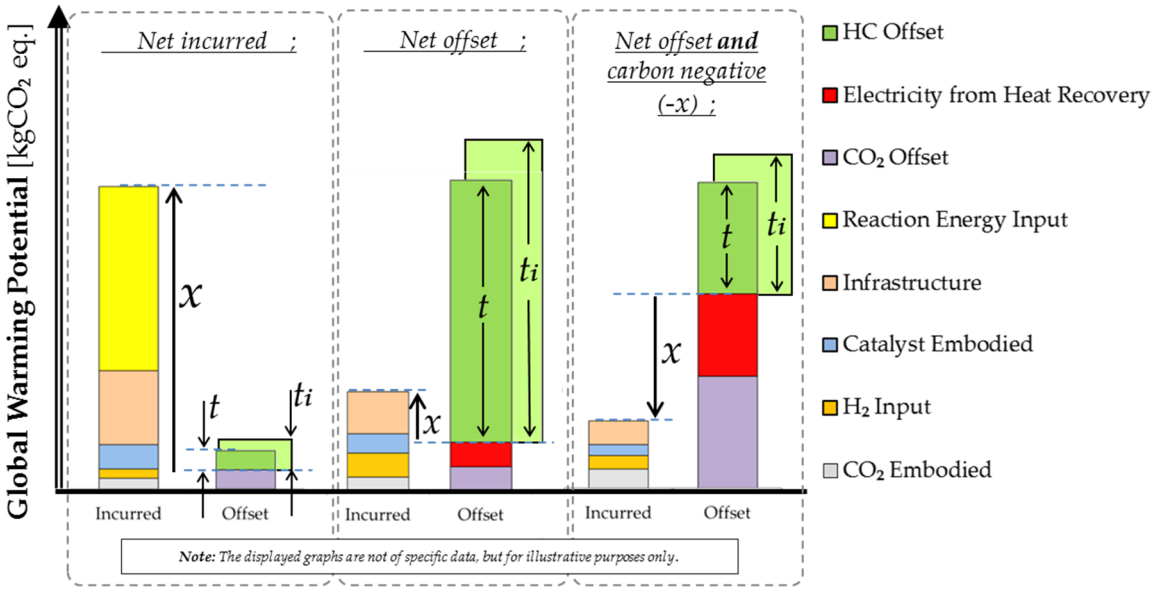
  Catalyst lifetime demands for the most part are quite low, thereby suggesting industrially-relevant 5000-hour catalyst lifetimes would most likely satisfy this target. With the reaming infrastructure of decades being acceptable in the context of multiple catalyst regenerations/installations occuring during this period.

Toxicity, freshwater eutrophication and metal depleting impacts remain if at all paid back, requiring many decades, even centuries, operation before an offset of the running process would be achieved. These are arguably unfeasible, leaving decision makers with the question of environmental trade-offs as the process is currently modelled. It is foreseeable that alternate and lower impact process design could occur in the future, however, it is likely that the impacts in these specific categories will always likely be high due to the high precious metal usage and its resultant environmental effects.

6.13 Assessing the Impacts of the RWGS-FT Products

The overall environmental balance of the laboratory process, as covered in the previous whole system assessment, is incurring impacts many orders of magnitude greater than any offset being achieved by the products. Therefore it follows that the resultant products formed via the RWGS-FT process will be of higher impact than the impacts of sourcing the same HC mix from existing sources.

As shown in Figure 6-22, the net impact of forming the products, x, can be considered the total incurred impacts in forming them, less any other offsets, i.e. CO_2 being immobilised from the atmosphere, and where applicable, the co-generation of electricity. This is then related to the impacts of the equivalent mix of products formed via traditional routes. This approach is in alignment to the methods noted in chapter 3 of this thesis, specifically section 3.8.2 and3.8.3, (page 64).



x = net impact of forming products; *incurred - offset*

t = impact of sourcing the same hydrocarbons from traditional routes

t_i = same as t, but for ideal catalyst product selectivity

$$\text{Relative product impact} = \frac{x}{t_i}$$

Figure 6-22 Overview of method used to compare the impact of forming products via the RWGS-FT route and those of traditional pathways.

With reference to Figure 6-22, in order to normalise between the tested catalysts, the ideal product distribution for the converted CO_2 is used. If the direct offset '***t***' were to be used, catalysts which produced longer chained –traditionally more impactful products – would be penalised over those which tended to produce mostly methane, a significantly lower impact product. To allow for this the ideal offset '***ti'***, is used, based on the converted quantity of CO2 being made into the ideal selectivity / product mix Thus the best performance is seen for catalysts with highest conversion of CO_2 to the most desired product mix.

The ratio of x/ti gives great insight into the performance of the process, since:

- x / t_i is > 1, the RWGS-FT is producing products with a higher impact.
- x / t_i < 1, lower impact products are being formed via RWGS-FT route.
- Futhermore, if x is negative, then this is a condition whereby the products are GHG net negative, x / t_i then displays how many times more negative (net offsetting) with reference to equivalent mix of traditionally sourced HCs.

The following sections look at the steps that require undertaking, implementable, and hypothetical, to reduce the impacts of forming the hydrocarbons. To either bring the impacts in-line, or better than, traditional routes.

6.13.1 *SCENARIO CASES FOR THE RWGS-FT PRODUCTS*

In an attempt to establish what steps would be necessary for the RWGS-FT catalysts to produce environmentally favourable mixes of hydrocarbons, a series of case scenarios are hypothesised:

- Reference: current laboratory setup (Figure 6-13, page 172)
- Scenario 2: improved 'lean' laboratory process, improved catalyst synthesis, gas recycling (Figure 6-16, page 185)
- Scenario 3: 'lean' process with exothermic process realisation, no heat in and recoverable heat out (Figure 6-17, page 187)
- Scenario 4: as scenario 3, however no recoverable heat, and infrastructure impacts 10 % of improved 'lean' model.
- Scenario 5: as scenario 4, but with recoverable heat for power generation.

Table 6-18 Impact of forming products via RWGS-FT versus existing routes.

a.k.a X /Ti values

Colour key:	>10,000 times impact		< 10 times impact but >1
	>100 times impact		Less impactful
	<100 times impact but >1 0		Less impactful and GHG negative

	Fe20	Fe10Pd1	Fe20Pd1	Fe30Pd1	Fe40Pd1	Pd1Fe20	Pd2Fe20	Pd3Fe20	Pd4Fe20	Fe_DEC_CNT	Fe@CNT	Fe@CNT-2.5 bar	Ideal FT Catalyst
Laboratory	31800	9474	7980	4950	3437	7983	6193	4831	4454	19940	5607	3801	1136
Scenario 2	571	169	142	87	59.6	142	110	85	79	359	99	66.0	17.8
Scenario 3	59	15.5	12.6	6.5	3.5	12.6	9.4	6.8	6.3	38.2	7.8	4.1	-1.3
Scenario 4	5.9	0.3	-0.1	-1.1	-1.6	-0.1	-0.3	-0.6	-0.5	5.3	-0.9	-1.4	-2.5
Scenario 5	5.2	-0.5	-0.9	-1.8	-2.3	-0.9	-1.1	-1.3	-1.2	4.6	-1.6	-2.3	-3.2

Table 6-18 provides a relative measure of how many orders a modelled process case scenarios are more, or less, impactful than traditional routes, as discussed in the previous section. Being dimensionless in nature allows for easy comparison between catalysts, including the ideal catalyst performance, with reference to the incurred impact of an equivalent mix sourced from traditional HC pathways..

Key findings are that at the laboratory the impact of formed products is many thousand times more impactful than existing routes. The move to a leaner setup, scenario 2, brings the impact to within a 100 for the best performing FePd and CNT catalysts.

A significant gain is seen when the exploitation of process heat is considered. For scenario 3, demonstrative of this gain is the ideal catalyst producing net negative products. If catalysts could be designed to approach that of the 'ideal' conversion and product distribution there is a potential for less impactful products via the RWGS-FT process.

Less impactful, and indeed mostly net negative products are achieved within the model once the infrastructure impacts are dropped to 10% of their present values.

For scenario 5, catalysts already shown to be negative-emittors are now capable of offsetting approximately twice the equivalent impacts; i.e. for every unit of GHG typically released for the production *via* traditional routes, now two units are being infact offset; representing a CO_2 sink.

This measure is to the production gate of the formed products, and does not take into account in-use combustion / potential emissions if used as fuel. However, if bound into pharmaceutical, polymer or composite forms these are potential GHG sinks.

6.14 CATALYST REGENERATION

As with all industrial catalysts extended operation times will eventually result in a reduction in the catalytic performance. Heterogeneous catalysts have the ability to be regenerated, purging them of soot, poisons, and other deposits adversely affecting the reaction performance. Regeneration is likely to occur several times in the life cycle of the catalyst, as shown in Figure 6-23. A conventional in-situ method of regeneration is an oxidation, or burn-off, of the catalyst surface. Catalyst regeneration occurs in the presence of high temperature and typically a more concentrated oxygen atmosphere. From the perspective of life cycle benefits for regeneration they require consideration in the context of synthesising new materials for substitution within RWGS-FT process.

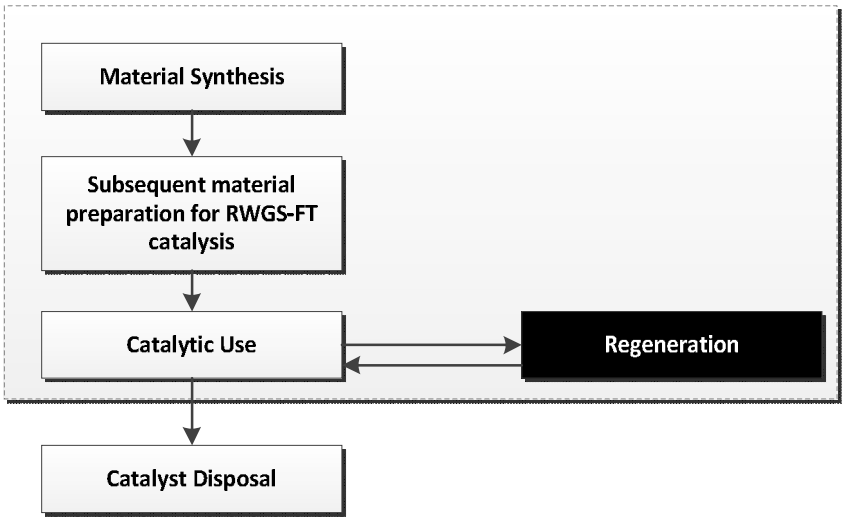


Figure 6-23: Boundary for comparing impact of new catalyst synthesis versus a regeneration step.

The proportional impacts of a regeneration step are higher for catalysts with the lowest embodied impacts. Figure 6-24, therefore, presents a worst-case scenario for the likely

contribution of regeneration, using the lowest impact silica based (Fe20) and carbon nanotube (Fe@CNT) catalysts, respectively. It can be deduced that the impact of regeneration is significantly lower than re-synthesis of catalysts, thus, providing reaction conditions return to their original performance this activity is always favourable in comparison to re-synthesis of catalysts. It must be noted that there is a possibility that the catalysts may undergo unrepairable degradation or irreversible poisoning. Thus more extended in-use operation of the catalyst is required to establish the time period between regeneration cycles, and on the general health of the catalysts over sustained operational periods; allowing a more accurate account of in-use impacts to be gained.

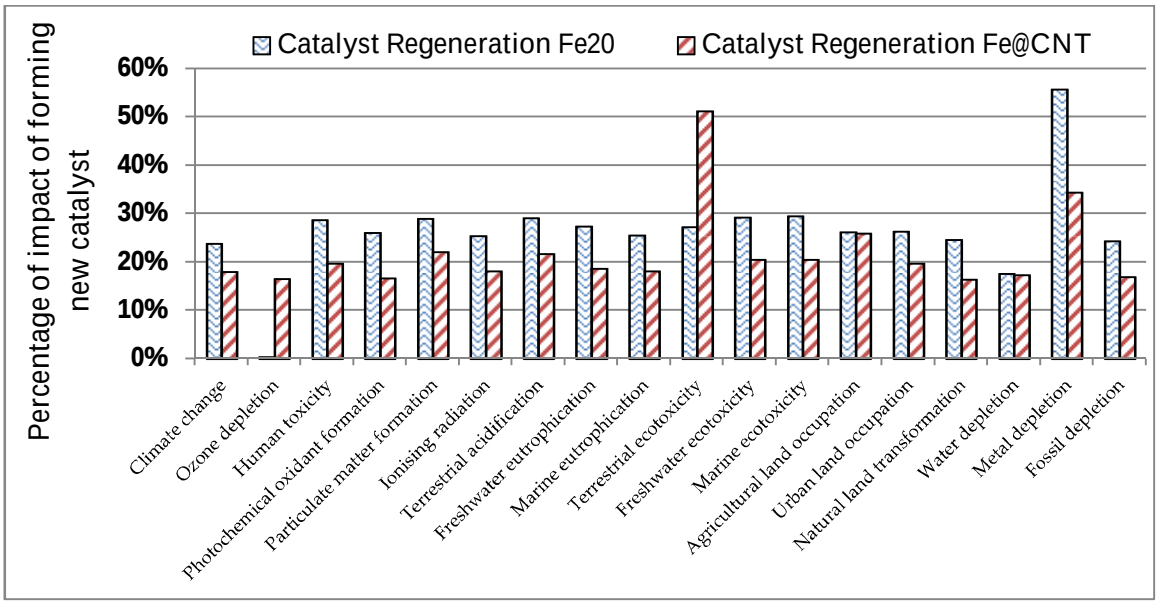


Figure 6-24 Catalyst regeneration step as percentage of the initial synthesis life cycle stages.

6.15 CONCLUSIONS AND RECOMMENDATIONS

In this chapter, a series of iron-palladium-silica and multi-walled carbon nanotube (MWCNT) catalysts were modelled relative to one another within a prototype reverse water-gas shift coupled Fischer-Tropsch (RWGS-FT) process. This process is demonstrating the ability to convert gaseous CO2 into hydrocarbon species up to chain lengths of seven carbon atoms, i.e. heptane. The work focused on the basis of their relativeoperational performance and net life cycle burdens.

Firstly was the net GHG emissions resulting from utilising CO_2 and its subsequent conversion into hydrocarbons. A schematic snapshot of the life cycle impacts is shown in Figure 6-25. In the extreme cases the best and worst overall LCA performance are witnessed by the best and worst performing catalysts during use. However, the effects of life cycle burdens show some favourable in-use catalyst e.g. Pd4Fe20 are overall poor-performing in the context of the overall life cycle. This finding is demonstrative of where a catalyst seems favourable in terms of operating performance, but this performance is achieved at a greater penalty than that which is being offset. This is an important consideration when seeking to produce a catalyst which minimises, and ultimately negates net environmental impacts of a process.

The two best performing catalysts were found to be Pd1Fe40, Fe@CNT, the former lowest loadings of palladium and were coupled with performing in the top three operational performances. Fe@CNT is the best of the two tested multi-walled carbon nanotube catalysts, it offers better hydrocarbon production in terms of displacing more impactful mixes of HC, however since a lower quantity of product is formed in comparison to Fe40Pd1 the co-benefits of process heat and indeed immobilisation of CO2 results in a marginal overall lower net life cycle benefit.

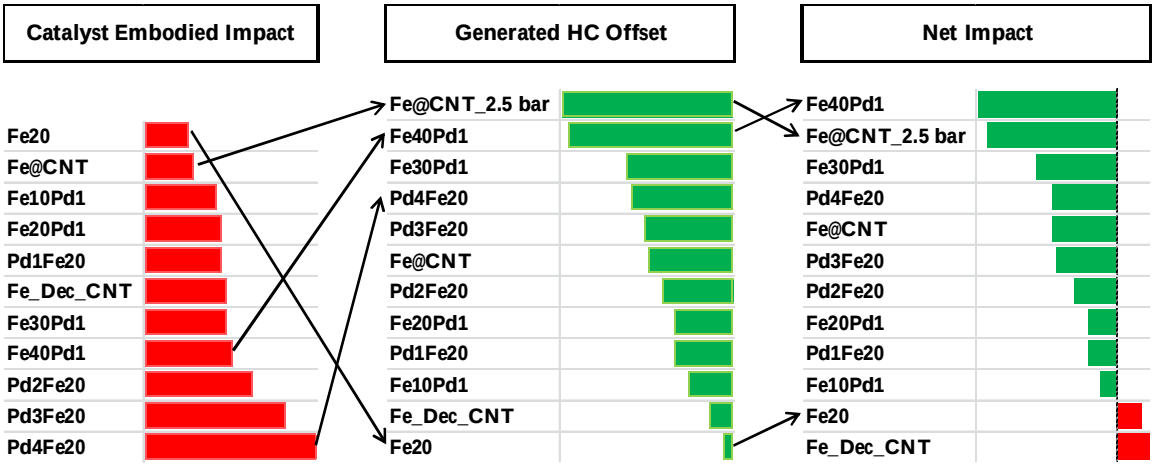


Figure 6-25 Relative GHG, red if emitting green is : incurred catalyst synthesis impacts (left), operational hydrocarbon equivalent offsets of different catalysts (centre), and the best overall life cycle performance of the catalysts (right).

Quantify the environmental effects that process operation across different reaction conditions have on the performance of the processes.

In the context of the overall life cycle impacts of the process, considering additional impacts to that of CO_2 equivalent emissions alone. It was found that CO_2 abatement can be considered to come at a cost to wider environmental impacts, with 12 out of 18 impacts worse for Fe40Pd1 and 14 out of 18 for Fe@CNT. The overriding factor contributing to these environmental impacts are due to the life cycle impacts of the infrastructure. At laboratory scale the increased burden from infrastructure can be appreciated since many auxillary, monitoring equipment is present, and the reaction vessels are generalist pieces of equipment rather than specifically made for the process at hand, thus carrying redundancies in terms of function and size. Environmentally beneficial outcomes appear across all impact categories once the relative impact of infrastructure is addressed, through either anticipated process improvement with scale, and E-O-L material recovery to mitigate initial embodied impacts.

A framework was developed, section 6.7, to investigate the life cycle benefits/penalties for operating the catalyst Fe@CNT (although could be any catalyst) at different reaction conditions, it was found that less catalysts performed better in the context of a balanced life cycle evaluating approach, it was shown that catalyst conversion performance alone was not in itself a sufficient translation of net life cycle performance. With full consideration, the optimum conditions in terms of GHG mitigation was found to be at 2.5 bar reaction pressures; already expected but further confirmed.

Determine the impacts of the formed hydrocarbon products from the assessed RWGS-FT route, compare with existing chemical production pathways.

At present conditions the hydrocarbon products formed are many orders of magnitude more impactful than traditional fossil-fuel based production routes. However, through feedstock gas recycling, the realisation of exothermic process potential, and a lowering of infrastructure equipment burdens; the potential for lower impact hydrocarbons in comparison to existing petrochemical routes are possible. Indeed for the best performing catalysts modelled under the best case scenarios, Fe40Pd1 and the Fe@CNT catalysts both show the potential for net negative GHG emissions, effectively offering the potential of products with a CO_2 sink.

In the context of CO_2 utilisation, how do the RWGS-FT processes perform, and how feasible is their implementation. Within this is the provision of targets in which the processes must reach in order to become carbon neutral.

Similarly to the previous aim, process enhancements are required in order for the processes to operate with environmentally beneficial performances. In comparison to existing hydrocarbon production routes, it has been shown that there is the potential for a process based on the catalytic performances of the RWGS-FT catalysts assessed to be GHG neutral within ~7 years of continual operation. Considering wider environmental impacts, the processes can also potentially offset other environmental impacts in addition to GHG impacts, the majority of which can be recovered within a one to two decades of operation. However, some impacts would require operation in order of a century to be life cycle neutral. The category metal depletion, arguably, never shows a likelihood of a return on initial embodied impacts due to catalyst metal usage.

6.15.1 *OVERALL LCA FINDINGS:*

- Energy use is prohibitively too high an impact, process must achieve thermally self-sustaining scales of operation.

- Recycling of feedstock gases are essential to prevent unnecessary high in-use catalyst operational impacts.

- Catalyst embodied impacts are far lower than the incumbent impacts of the operational infrastructure. However, the recovery of palladium metals, as detailed in chapter 5 significantly improve catalyst embodied impact, lowering the bar in reaching net favourable environmental performances.

- Infrastructure impacts relative to the functional unit are too large as they presently stand. Addressing this required a combination of lowering the specific infrastructure impacts (anticipated through larger process scales), additionally E-O-L constituent material recovery would mitigate much of the embodied impacts of the running equipment.

6.15.2 *RWGS-FT RECOMMENDATIONS*

With the LCA indicating a potential benefit obtainable from this process it would be advisable to continue this process along to the next stage of development, i.e. a pilot scale process. Initially from a theoretical, design based approach, establishing the material impacts of the operational equipment; seeing where materials would be minimised by increasing scale and a more comprehensive grasp of the pressure impacts which are presently founded on theoretical calculations. Additionally, the increased scale would allow the determination of the point in which the process would become auto thermal, not requiring process heat input to be validated, and furthermore how much energy could be truly extracted from an operational unit.

6.15.3 *LCA CONTRIBUTIONS AND FUTURE RWGS-FT WORK*

Parts of the work detailed in this chapter have been incorporated into a published study (Griffiths *et al.* 2013b). The co-authors of the study are continually seeking to improve the FT process, in terms of implementable changes at the R&D stage the dominant impacts of palladium metal in the iron:palladium catalysts were targeted for further work. Catalytic performance has also undergone improvements, with even iron-only catalysts performing better than any material detailed within this chapter.

The collaborators have used different pore-sized silica substrates the catalytic performance of Fe20Pd0 and Fe20Pd1 were improved. Indeed, the new formed catalysts are better than any previously assessed, with increased CO_2 conversion and selectivity towards longer (non-methane) hydrocarbons, see Figure 6-26. Further work would be to appreciate more comprehensively the life cycle impacts of silica to fully validate the benefits.

LCA is therefore lagging behind the rate of catalytic development progress of this particular RWGS-FT process, however, the major findings and outputs are still being incorporated into the decision-making. The LCA results also stand apart from the specific assessed process, informative for other seeking to appreciate the inherent and prohibitive life cycle activities preventing, at present, favourable environmental returns from the process.

Wider implications of the LCA work can also be considered to provide much needed in-use phase assessments of ENMs performing in existing, in this case Fischer-Tropsch fuel, applications with wider and present-day economic relevance. It has also been possible to demonstrate that process design as well as catalyst choice will require consideration, and that follow-on work should be conducted on the kinetics of the reaction and reactor setup to better realise, and explore the utilisation of, process heat generation.

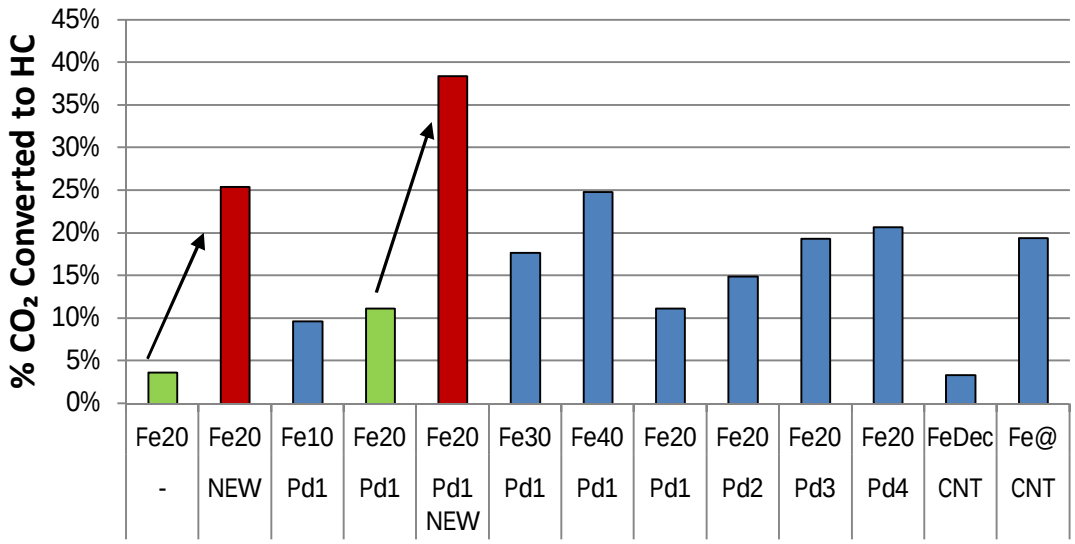


Figure 6-26 CO_2 conversion improvement (red) from equivalent catalyst loading (green) for the 'new' catalyst made on altered silica substrate.

Chapter 7: AQUEOUS ELECTROCHEMICAL REDUCTION OF CO_2

USING NANO-CATALYST ELECTRODE COATINGS

This chapter is concerned with an electrochemical route of CO_2 conversion, using electrode coatings consisting of gold with palladium shell nanoparticles. In the context of using CO_2 as a feedstock, the LCA results show this is- *in the best modelled cases*- beneficial from the perspective of many of the measured environmental impacts, including (but not exclusively); GHG, fossil fuel depletion, cumulative energy demand, land usage, and human toxicity impact categories. The extent of environmental benefits is increased once, a more streamlined electrode synthesis route is considered, and an end-of-life metal recovery stage included. However, even for best cases, there are impacts that are inherent for: ozone depletion, particulate matter formation, terrestrial acidification, freshwater ecotoxicity and metal depletion impacts.

The lowest cradle-to-gate impact catalyst does not provide the best overall life cycle performance. The more impactful catalyst, (owing to higher gold content) 'pays back' sooner and across more impact categories due to much enhanced in-use CO_2 conversion. The system is feasible providing specific criteria are met:

- A low-impact electricity source is used to operate the cell - and if used during catalyst synthesis steps will significantly lower environmental payback period.
- Electrode can sustain operational performance for; a minimum of 3 months to become carbon (greenhouse gas) neutral; approximately 6 months to cover the majority of other environmental impacts; and 5 years to cover all apart from metal depletion incurred environmental impacts.
- An end-of-life strategy for retrieving the precious metals encased in the catalyst / electrode(s) surface. However, metal depletion impacts are arguably always irretrievable, with 30 year lifetimes required even when 70% of metal is modelled to be recovered.

7.1 INTRODUCTION ELECTROCHEMISTRY LCA OVERVIEW

This chapter is concerned with research being conducted into the electrochemical reduction of CO_2 -in an aqueous solution - using nanometal catalysts. This LCA work is founded upon the collaborators publications detailing their progress in this area (Plana *et al.* 2010; Montes de Oca *et al.* 2011; Celorrio *et al.* 2012a; Plana *et al.* 2013). The research is primarily concerned with optimising electrochemical catalysts for the effective conversion of CO_2 into useful compounds. The specific process investigated is an electrochemical cell, utilising electrode coatings consisting of nanoparticle gold, with nano-palladium shells dispersed onto nano-sized carbon black.

Electrocatalytic reduction of CO_2 using nanoscale active electrodes is an emergent research area (Kondratenko *et al.* 2013). The field is presently concerned with identifying and optimising the best performing catalysts capable of CO_2 conversion to carbonaceous products; the LCA work contained in this chapter is complimentary to this phase of research and development. To date, no examples of LCA being used to guide catalysis development in the field of CO_2 electrochemistry has been found in the literature. LCA has been used to determine the impacts of forming the electrode materials, and further expanded to cover the in-use catalytic reaction, and a likely end-of-life phase. This study will lay benchmarks within the field, balancing impacts of using precious metals and intensive synthesis pathways against the potential environmental offset achievable through this CO_2-utilisating and chemical-producing route.

CO_2 Electrochemistry Background: Electrochemical CO_2 reduction is a process that has been investigated for numerous decades, such examples include continuous reactor setups investigated in the 1980's (Dewulf and Bard 1988). In light of mounting pressure to tackle rising CO_2 levels a resurgence in the field is occurring. The publications related to CO_2 electrochemistry and characterisation of materials, operating conditions and performance gains are numerous. Jitaru (2007) argues that the increasing patents in the field indicate a mounting interest and acceleration of technology development, however, the full environmental performance of such a system has yet to be fully explored. It is hoped that this LCA work will be a stepping-stone towards a better appreciation of environmental issues within the field.

Recent review papers of Jitaru (2007) and Spinner *et al.* (2012) details recent progress in CO_2 utilisation *via* electrochemical conversion processes. Highlighted within these reviews the potential advantages an electrochemical route would offer over other thermal hetero-catalytic based reactions are outlined, these include:

- higher efficiencies, since not limited to conventional enthalpies of reaction, electrons are supplied directly to the molecule surfaces.
- more control over process surface-reactant interaction, resulting in more tailorable control and increased selectivity towards target products.

For electrochemical CO_2 conversion, three predominant pathways are being explored: gaseous, non-aqueous (solid-oxide), and aqueous phase routes (Spinner *et al.* 2012). A technique falling in the latter – aqueous phase - category was investigated in this work. Specifically, a laboratory-scale electrochemical cell operating with a CO_2 saturated electrolyte solution, and a working electrode with a novel nano-metal active coating. Using nano-coatings for the electrode surface have two main benefits: reduced precious materials usage; with less 'wasted' within bulk material and not participating in electrochemical activity, and enhanced surface chemistry, boosted catalytic, effects at the nanoscale (Kim and Park 2013).

Copper electrodes have been identified as very promising CO_2 electrochemical catalysts (DeWulf *et al.* 1989) however these present high overpotential –electricity demands - and selectivity towards desirable compounds is proving a technical challenge to date (Peterson *et al.* 2010). Furthermore, sustained operational performance has faced issues such as deactivation after a few operating hours (Li and Kanan 2012), and copper dissolution from electrode and poisoning of catalyst surface (Spinner *et al.* 2012). Many conclude aqueous based electrochemistry will only be feasibly adopted once improvements are made to the performance and operating currents required to produce products (Spinner *et al.* 2012). The catalyst electrodes investigated in this work was conducted on a potentially more resilient electrode coating, which have to date been tested for longer durations than the reported 'drop-off' in performance periods, offering the potential for advancing more *via*ble catalytic solutions to the field.

Process Products: Due to the early stage research and diminutive scale of this process, the exact measured presence and content of the formed products has not been established. However, hydrogen production has been measured implicitly, the other *very likely* products as reported by others in the field of electrochemical reduction of CO_2 (Whipple and Kenis 2010; Taheri Najafabadi 2013) are one or a mixture of carbon monoxide (CO), formic acid (HCOOH), and methanol (CH_3OH): all potential products are industrially relevant, with multi-scale adoption in cross-industry applications; therefore economic and supply chain demands are drivers in addition to greenhouse gas abatement benefits of atmospheric CO_2 immobilisation.

- **Chapter Contribution:** LCA quantifies the current laboratory process setup with a view of what impacts would still be prevalent in a larger scale: pilot to industrialised adopted processes. Major highlights include identifying where major impacts lie, which of these could be reduced/avoided, and the technical performance targets to be met in order for the life cycle impacts of the operating catalysis process to reach carbon, and other environmental impacts; i.e. setting the criteria for the process to be a *via*ble environmental CO_2 utilisation process.

7.2 LCA AIMS FOR ELECTROCHEMICAL PROCESS

The overarching goal of this LCA work is to provide a frame of reference in the context of the overall environmental performance of the materials and processes at work within an electrochemical process of CO_2 conversion. Furthermore, to assess the early laboratory process to establish its feasibility in terms of effective CO_2 utilisation. Thus the main aims of this work are in-alignment with all four thesis objectives:

Objective 1. Establish the environmental impacts of forming the nanomaterials

Objective 2. Establish the life cycle impacts of the developed CCU processes, and report on the environmental feasibility of further technology development

Objective 3. Communicate to technology developers key life cycle results for action

Objective 4. Communicate wide environmental impacts

7.3 STUDY SCOPE: SYSTEM BOUNDARY

The LCA was conducted in-keeping with the adopted approach used throughout this thesis, in accordance to ISO standards (ISO 2006a; ISO 2006b). The assessment work within this chapter is two-part, covering the gate impacts of forming the gold-palladium nanoparticle electrode catalytic coating materials, and secondly to assess the use of these electrodes in a measured working cell, where the impacts of forming carbon-containing commodity chemicals are compared against reference industrialised routes of manufacturing these chemicals.

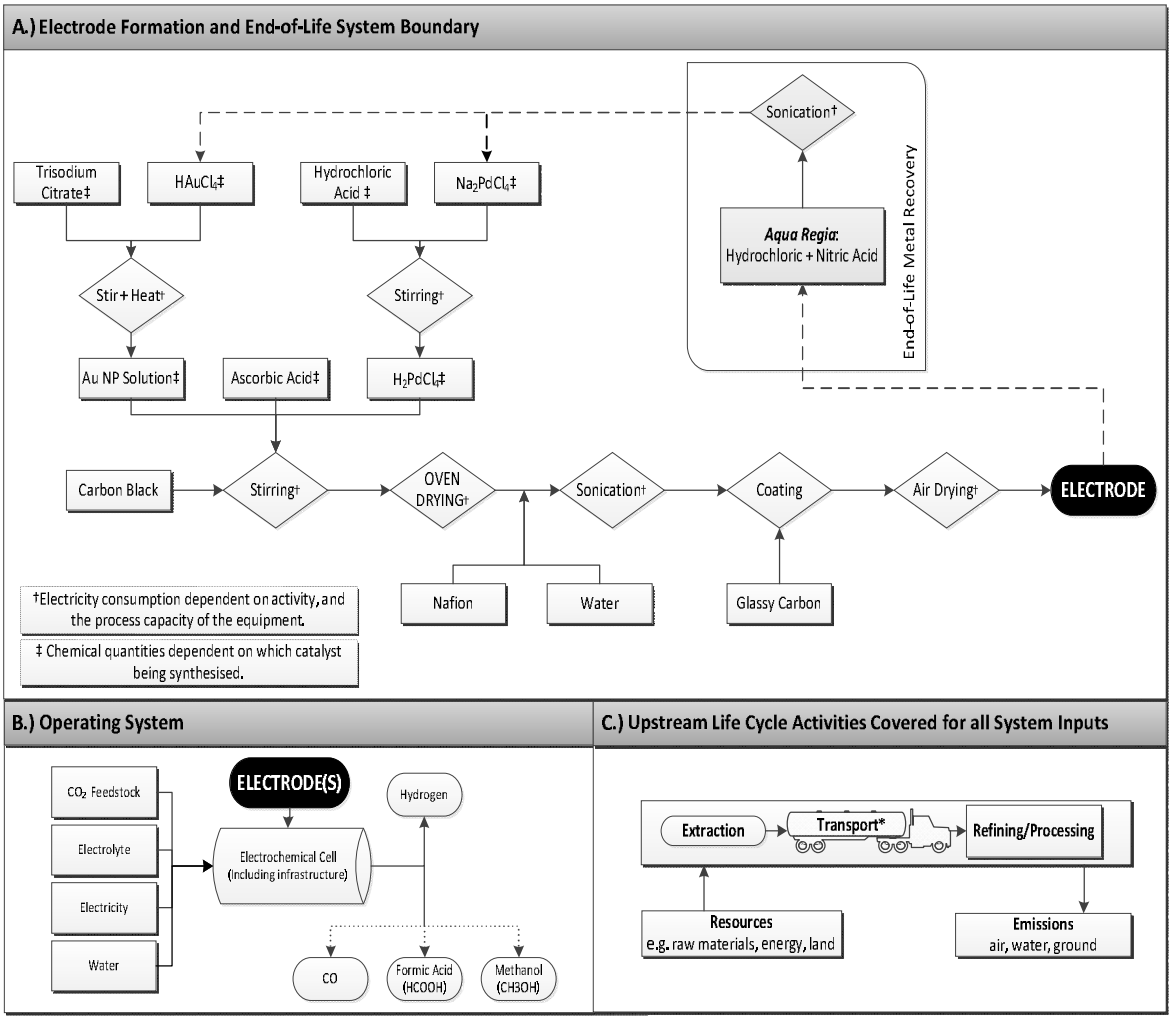


Figure 7-1 System Boundaries of LCA work: a. electrode coating formation, b. the operating electrochemical cell, and c. the scope of all process flows covered.

The life cycle coverage of this process has been expanded to cover an end-of-life processing stage, for both the formed electrodes and the infrastructure componentry devices once they have reached the end of their serviceable operational lifetimes.

The precious metals on the surface of the electrodes are targeted as *easily* recoverable deposits. The static and non-dispersive nature of the electrochemical process, specifically electrode operation, will likely result in physical dissolution and retrieval of the metal constituents being achievable activities. . The modelling of major constituent components of the capital infrastructure equipment recycling is also considered. Thus from a life cycle perspective the scope is from cradle-to-grave.

7.3.1 *FUNCTIONAL UNITS*

Three distinct yet related function flows are reported in this work:

1. For the technology developer; the gate impacts of producing the electrode.

2. For process development and comparison with other systems; the per hour operation of the electrochemical cell.

3. Wider context and environmental performance; the impacts arising per unit of CO_2 electrochemically converted, either reported as a ratio to other impacts, or stated as a 1 kilogram quantity.

7.4 ELECTRODE COATINGS FORMED

The materials assessed in this work are core-shell (CS) nanoparticles; gold cores with shells of palladium. Each gold core is 20 nm in diameter, the differentiation between types is due to the thickness of the palladium shell; 1 nm for CS1, and 10 nm for CS10 respectively. The formed nanoparticles (NP), properties are shown in Table 7-1, are deposited onto porous carbon black substrate before adhesion to the final electrode surface the material.

Table 7-1 a.) Composition of formed materials, from (Celorrio *et al.* 2012b).,

Nanoparticle	Pd shell thickness (nm)	Particle diameter (nm)	NP loading on carbon black (wt %)
CS1	**1.3 ± 0.1**	**21.8 ± 1.1**	**15.0 ± 1.9**
CS10	**9.9 ± 1.1**	**38.9 ± 1.5**	**17.5 ± 1.4**

b.) The carbon black support used (Celorrio *et al.* 2012b; Cabot Corporation 2013)

Descriptor	Particle diameter (nm)	Surface area (m^2/g)	Pore volume (cm^3/g)
Vulcan XC-72R	**30 to 60**	**218**	**0.41**

7.4.1 *ELECTRODE COATING PROCESS STEPS:*

The synthesis steps for both CS1 and CS10 are identical, the exception lies in the quantity of gold and palladium required to achieve the resultant shell thicknesses. The full synthesis pathway of the catalyst synthesis is found in (Celorrio *et al.* 2012b); Plana *et al.* (2013) and within the accompanying APPENDIX G:, however, the stages can be summarised as follows:

1 Synthesis of a solution of gold nanoparticles,

2 Mixing of nano-gold solution with palladium solution to form desired nanoparticles.

3 Binding of NPs with 80 mg carbon black to produce colloidal suspension

4 Suspension is oven dried to produce a powder nanomaterial compound.

5 2 mg of dry powder is mixed with 15 µL Nafion (10% aqueous dispersion) and 500 µL of de-ionised water – resulting liquid is termed the 'ink'

6 10 µL of ink deposited and left to dry onto glassy carbon electrode; ready for use.

7.5 THE OPERATING ELECTROCHEMICAL CELL

The formed CS-based electrode is used in conjunction with a platinum electrode to complete the system's electrochemical circuit. The operating cell was for a small-scale laboratory setup The LCA work has modelled the cell in its simplest, yet still fully functional, form. To this end the three-electrode laboratory setup, as shown in Figure 7-2, has been covered omitting the third, reference, electrode.

A reference silver chloride electrode is used in the laboratory setup; this is to accurately measure the potential voltages to calculate the current flow at the working electrode. It is beyond the scope of this thesis to cover the mechanism and principles of electro-analytical chemistry. Whilst the use of a reference electrode is essential when appreciating the precise performance and characteristics of the cell, it is not required in order for the chemical conversion of CO_2 to take place.

The working electrode – coated with either CS1 or CS10- and the counter platinum electrode are placed within an electrolyte solution 0.1 molar concentration of sodium sulphate solution, pH 4, which had been saturated with CO_2 by passing the gas through the solution.

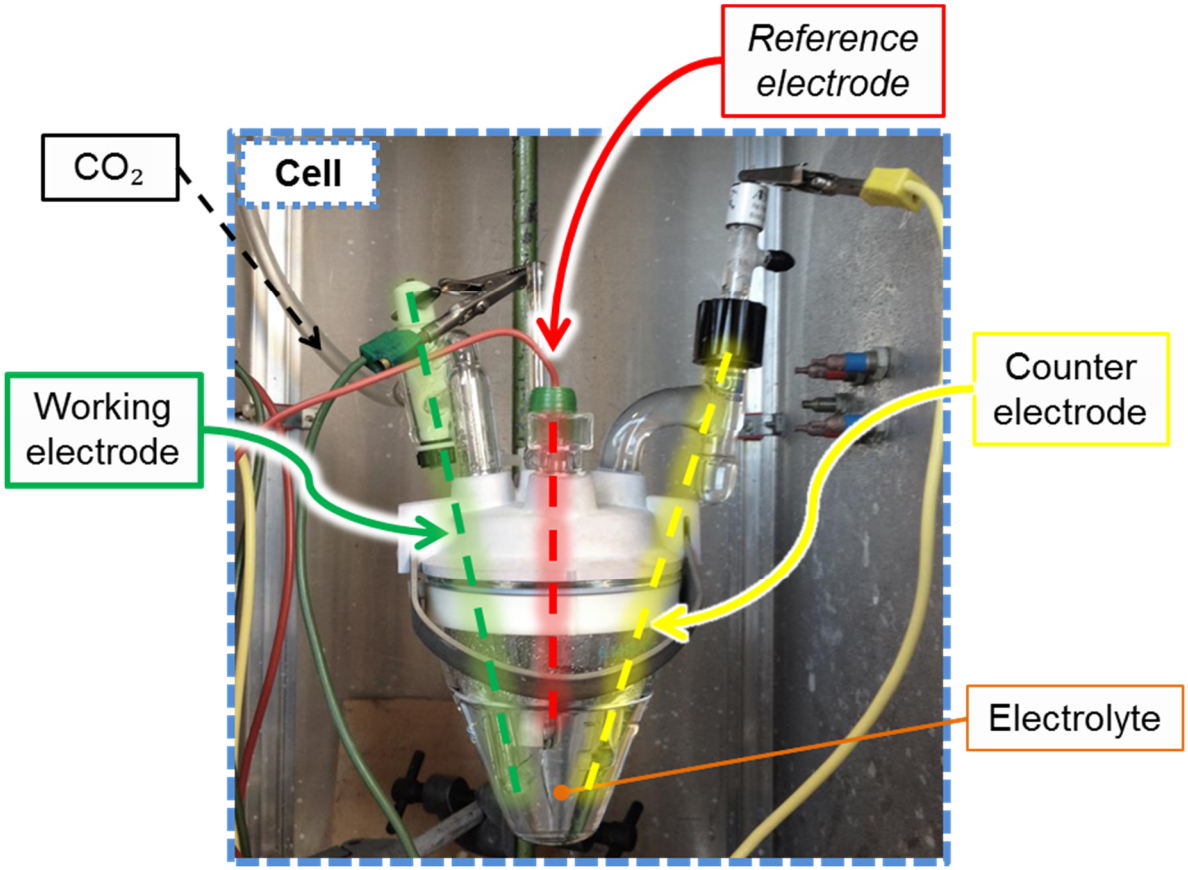


Figure 7-2 The electrochemical laboratory setup. All electrodes connected to a potentiostat (not shown). Picture adapted from one taken by Dr Daniela Plana.

The overall modelled working electrochemical cell is thus:

- the working electrode, a glassy carbon material in which either CS1 or CS10 catalyst coatings are applied.
- a counter platinum electrode.
- the potentiostat: providing electrical current to the cell.
- electrolyte solution: the medium necessary for ion-exchange and CO2 delivery to the electrode surface.

7.6 ELECTROCHEMISTRY PROCESS INVENTORY DATA

The inventory data collection is concerned with four predominant elements, the:

- chemical, materials, equipment and energy usage involved in electrode preparation,
- operation of the electrochemical cell,
- end-of-life metal recovery stage, and
- benchmarking the industrial production routes for comparison with the formed products.

7.6.1 *INVENTORY FOR ELECTRODE INK SYNTHESIS AND DEPOSITION*

Inventory data covers the capture of ink formation as performed at the laboratory scale. The coverage is for all upstream flows and processes needed, within and outside of the confines of the lab, to produce the final deposited electrodes for use.

Table 7-2 Inventory data related to electrode coating synthesis*

Chemicals & Materials	Equipment*	Energy
hydrochloric acid **nitric acid** **trisodium citrate** **ascorbic acid** **gold** **palladium** **carbon black** **nafion** **de-ionised water**	**mechanical stirrer** **hot plate** **oven** **sonicator**	**UK electricity mix, or** **offshore wind generation**
***Devices which do not play a direct part in the functionality of the electrochemical cell are not accounted for, e.g. mass balances, general laboratory glassware and analysis equipment.		

7.6.2 *ALLOCATION FOR FINAL FORMED CATALYSTS*

The functional unit used is for one working electrode, and thus the differing quantities of chemicals are used to produce the desired CS1 and CS10 composition. At the laboratory scale small quantities are used to produce even smaller final deposits on the electrode surfaces.

The total dry weight of synthesised material amounts to approximately 100 mg, whereby only 2 mg is required per ink synthesis. Furthermore, the 2 mg of used powder was dispersed in a 510 µl solution, with only 10 µl ultimately required for final electrode coating. Thus the allocation of total synthesis impact is approximately 1 ÷ (50 × 50), or one part in 2,500 of the total process synthesis impacts measured.

7.6.2.1 Precious metal usage

Gold, palladium and platinum datasets are found within the Ecoinvent Database v2.2 (2010), and modelled as coming from a production mix, adapted where necessary, to be best representative of the current global supply and recycling rates. The gold and palladium are not used in their primary pure elemental form but instead as solutions of chloroauric acid ($HAuCl_4$) and dihydrogentetrachloropalladate (H_2PdCl_4) respectively. The formation impacts of these materials, were modelled from literature sources and the constituent precursor reactants - predominantly exothermic reactions involving hydrochloric and nitric acid dissolution - calculated *via* mass balances and stoichiometry.

7.6.2.2 Recovery of precious metals

Gold, palladium and platinum metals are highly unreactive, however, they can all be dissolved within a concentrated solution of hydrochloric acid and nitric acid, a.k.a. aqua regia. Since the nanoparticles are bound to carbon black, which in turn are adhered to the electrode, an agitation stage to break the materials loose is very likely to be needed. The agitation of the electrodes has been assumed to occur in a sonicator. Within the LCA metal recovery at the electrode is modelled as followed:

1. Dissolution of electrode coating in an acid bath consisting of aqua regia; three parts nitric acid to one part hydrochloric. Quantity dependent on metal being dissolved to form respective metal solution:

	Moles of aqua regia to dissolve metal				Mass (g)	Volume (ml)
Electrode	**Au**	**Pd**	**Pt**	**Total**		
CS1	**1.3E-07**	**1.0E-07**		**2.3E-07**	**4.0E-05**	**2.7E-05**
CS10	**3.1E-08**	**3.9E-07**		**4.2E-07**	**7.3E-05**	**4.9E-05**
Counter Pt			**2.5E-07**	**2.5E-07**	**4.3E-05**	**2.9E-05**

2. Resultant mixture is sonicated, assumption: using existing laboratory sonicator, 15 minute period would be required, only 20 electrodes could be processed at a time.

3. Separation of palladium, gold, and platinum would be achieved by an acid precipitation stage.

This activity, albeit deemed feasible, has not been conducted in the laboratory. Therefore assumptions have been taken, whereby the maximum recovery of electrode metals is set at 70%. This percentage recovery is to account for potential losses, and the amount realistically recoverable, further work will be necessary to determine the actual amount of obtainable metal once the overall process has been fully optimised for the electrochemical end application.

7.6.2.3 Carbon black

Satisfactory inventory dataset for the used nanoparticulate pure carbon, or carbon black, was found in Ecoinvent Database v2.2 (2010), with an accompanying report for carbon black entry in Althaus *et al.* (2007). This is in alignment with information on the oil furnace synthesis route is provided in the Kirk-Othmer Encyclopaedia of Chemical Technology (Wang *et al.* 2000), and that reported by the manufacturer Cabot Corporation (2013) of the specific carbon black VULCAN XC72R.

7.6.2.4 Material synthesis electricity consumption

For the synthesis, as shown in Figure 7-1 (page 215), stirring, oven drying and sonication stages occur during the formation of the catalyst coatings. An optional forced heated air drying is performed, *via* a consumer hair dryer, however early LCA scoping work found this prohibitively energy intense, especially since natural air drying overnight produced the same final electrode coated surface.

Table 7-3 provides an account of the electricity consumption during synthesis, a lean case is presented for the oven drying stage, this represents the capacity of the device to dry more than one batch at a time based on its physical dimensions. The assumption taken is that the oven could fit 96 crucibles filled with the pre-powder synthesis chemicals, the reduced volume of CS10 by a factor of ~1.6 results in 156 batches.

The assumption for lean oven drying is crude, however, its deemed a realistic case for sufficient air flow around oven to heat crucibles uniformly, and since the assumption is taken for both CS1 and CS10 based on their relative volumes, then any erroneous results from the assumption will be the same for both. No lean reduction in electricity usage for sonication and stirring activities were taken. Minimising these activities would require laboratory based investigation for the resultant effects of synthesising the materials via adapted stirring and sonication steps.

Table 7-3 Summary of electricity consumption by different processes during the catalyst synthesis and deposition.

	CS1 - Total consumption	CS10 – Total consumption
Stirring	**0.396**	**0.396**
Sonication synthesis	**0.0143**	**0.0143**
Oven drying	**10.2 (lean = 10.2 / 96)**	**10.2 (lean = 10.2/156)**
Sonication metal retrieval	**0.0215 – for 20 electrodes**	**0.0215**

Related to total synthesis vat and not individual electrodes. See synthesis steps of section 7.4.1 (page 217).

7.6.3 *INVENTORY DATA FOR OPERATING ELECTROCHEMICAL CELL*

This LCA models the working electrochemical cell in its most basic and functional form, covering elements that are necessary for the conversion of CO_2 into the formed products. However, the LCA does not cover auxillary equipment with functions separate to the primary electrochemical process; such as monitoring and sampling equipment.

Table 7-4 Inventory Data Related to operation of electrochemical cell

Material	Equipment	Energy
Chosen catalyst **CO_2** **Electrolyte** **Platinum** **Graphite**	**Potentiostat** **Electrodes** **Cell**	**UK Electricity Mix, or** **Offshore Wind Generation**

7.6.3.1 Platinum Counter Electrode

In order for an electrochemical cell to work, an anode and cathode are required, receiving and donating charge respectively. For CO_2 reduction, the working electrode is a cathode supplying electrons to form new molecules, suitable anodes for this process (and indeed many electrochemical processes) are platinum-based (Zoski 2007).

A platinum counter electrode, prepared by a similar method to the CS coatings via an electroless deposition of an ink onto a glassy carbon electrode is detailed by Lin and colleagues (Lin *et al.* 2010), and is 34.55 $\mu g\ cm^{-2}$. The surface area of a typical counter electrode for use in laboratory-based electrochemistry is approximately 0.7 cm^2 (Bio-Logic Science Instruments 2013), the resultant mass of platinum used is thus 24 μg.

Other electrode synthesis pathways offer the potential for lower mass depositions of platinum, whilst maintaining similar electrochemical performance (Lin *et al.* 2011), these would offer >85 % reduction of primary materials. The use of different synthesis pathways for electrode construction (from a review there are six or more techniques (Lin *et al.* 2011)) open up wider system boundaries, outside of the scope and thus unmeasured for this investigation.

This material reduction has been incorporated as an upper limit for the purposes of modelling a lean counter electrode. Lean platinum electrodes will be synthesised following the same procedure, but will have 85% less metal content to fulfil the same function and allow the cell to operate.

7.6.3.2 Potentiostat

A potentiostat monitors and supplies the electrical current to the electrodes. In the absence of data provision by the manufacturer of the device, it is modelled within this work from an open-source wiring diagram and bill of materials of a similarly capable potentiostat device, detailed in Rowe *et al.* (2011). The circuit board and constituent materials have been broken down into contributing parts, Appendix G.5, the respective electronic components and devices, e.g. resistors, capacitors, transistors, LED displays, have been accounted for using Ecoinvent Database v2.2 (2010).

At the laboratory scale one potentiostat is used per working cell. For the lean account , providing a more indicative account of a larger operating scale, the potentiostat embodied impact has been allocated on the deliverable power achievable from the device. In this case the cells use between 0.21 – 0.23 mWatt (see

Table 7-5) but the potentiostat can deliver approximately 8 Watt (*P=IV; 800mA, 10V*); based on similar manufactured devices (IVIUM Potentiostats 2013). Thus, the potentiostat device could theoretically power 35,000 of these cells; as such, this case has been used to model the lean approach.

7.6.3.3 Carbon electrode

The electrode catalysts are coated onto a 'glassy' carbon electrode, named due to its high polished mirror-like finish. The physical dimensions dictate approximately 10 mg of this material is required per electrode, however, datasets for the exact material have not been accessible. The material that most closely matched this was graphite, specifically 'battery grade graphite' within Ecoinvent Database v2.2 (2010).

7.6.3.4 Electrochemical cell electricity consumption and product formation

The electrochemical cell power consumption was measured empirically at the source, as was the efficiency of the operating electrodes (Plana *et al.* 2013), this data for both

catalysts is shown in Table 7-5. The Faradaic efficiency is an indicator of the electricity being delivered into forming the intended products, in this case carbonaceous compounds and 'lost' in forming the co-product hydrogen or via any other losses such as cell resistance

Table 7-5 Electricity consumption for the operating cells

Electrode	Power (W)	Electricity Consumption mWh (milliwatt hour)	Faradaic Efficiency
CS1 (Pd28)	**2.1×10^{-4}**	**12.6**	**92 %**
CS10 (Pd82)	**2.3×10^{-4}**	**13.8**	**41 %**

The presence of hydrogen was detected at the anode, however no exact determination of products formed from CO_2 have been measured. The products are thus hypothesised from similar work conducted in the field (Whipple and Kenis 2010; Taheri Najafabadi 2013). By appreciating the electrochemical reaction mechanisms for the different products the supplied electricity gives an account of the quantity of products formed, which varies dependent on the product (Zoski 2007). Figure 7-3 provides an account of maximum values if only one product were to be formed in isolation, via the following electrochemical reactions:

On the anode:	Likely products on the cathode:	
$H_2O \rightarrow ½\ O_2 + 2H^+ + 2e^-$	**Carbon monoxide**	**$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$**
	Formic Acid	**$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$**
	Methanol	**$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$**

The datasets for the formed chemical products come from Ecoinvent Database v2.2 (2010), the supporting documentation for these datasets Althaus *et al.* (2007) were found to be in close alignment and relevant to the most reported methods of production, detailed in Table 7-6.

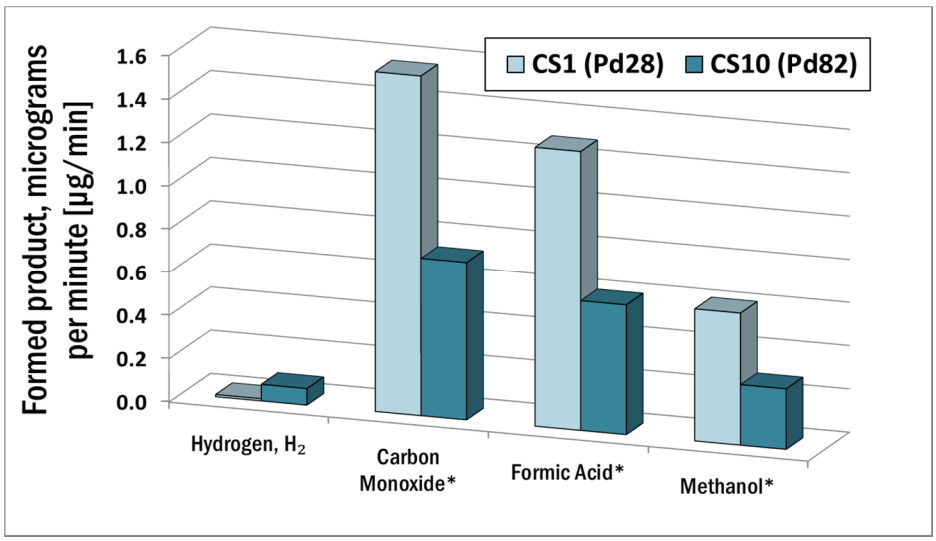


Figure 7-3 The quantity of formed product per minute of reaction, dependent on the catalyst used.

Table 7-6 Industrial manufacture route for three likely products formed during the electrochemical reaction, as modelled in this work.

Product	Established Industrial Production Route
Carbon Monoxide (CO)	**Co-product of syngas along with H_2 Part combustion of carbon compounds, e.g. coal and heavy oil distillates. (George 2000; Althaus *et al.* 2007)**
Formic Acid (HCOOH)	**69 % from methyl formate (carbon monoxide + methanol)** **31 % from butane (from refinery) (Reutemann and Kieczka 2000; Althaus *et al.* 2007)**
Methanol (CH_3OH)	**From natural gas steam reformation predominant, Syngas – anaerobic digestion, also of interest (Fiedler *et al.* 2000; Althaus *et al.* 2007)**

7.7 LCIA: RESULTS AND DISCUSSION

Life cycle activities are assessed using the ReCiPe midpoint and cumulative energy demand (CED) impact assessment methodologies; described in chapter 3 of this thesis.

7.7.1 *CO_2 USE VERSUS PRODUCTS FORMED*

When assessing CO_2 utilisation technologies, an important criterion to meet is that products formed are more environmentally valuable than the penalty of the captured CO_2 feedstock needed to make them. For the three likely formed products hypothesised for CS1 and CS10 this condition has been met, as shown in Figure 7-4.

The global warming potential (GWP) benefit of CO_2 immobilisation plus emissions avoided in this category by *not* synthesising products via traditional routes (Table 7-6, page 226) leads to very net negative emissions. When synthesising carbon monoxide and formic acid, the penalty of capturing the CO_2 is outweighed – by many orders of magnitude - by the avoided emissions.

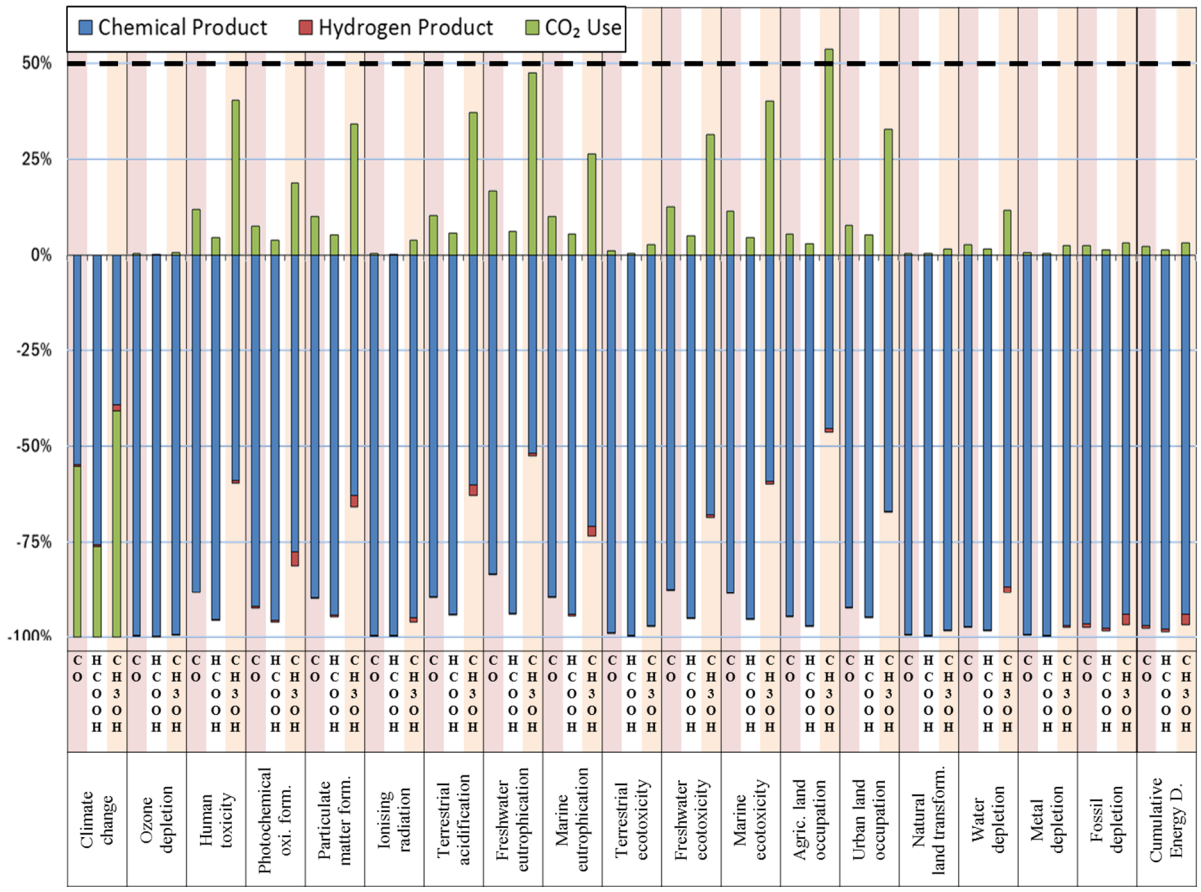


Figure 7-4 Impacts of CO_2 consumption versus the formed product. Same irrespective of catalyst used, albeit CS1 will be operating at a higher conversion rate.

The advantages of producing methanol is less clear cut, with over half the measured impact categories showing significantly less net CO_2 conversion benefit; i.e. the converting technology would have to perform within a smaller band for process to be environmentally net beneficial. Additionally, the sole exception for CO_2 impacts not being outweighed by the formed product is seen for methanol in the agricultural land occupation category. By taking a mix including a third equal parts of CO, HCOOH and CH_3OH it is trusted that a fairer representation of the likely transformation benefits of the electrochemical process has been achieved.

7.7.2 *ELECTRODE COATING IMPACTS*

The LCIA results of forming both CS1 and CS10 electrode coatings are shown in Figure 7-5. The impacts of both catalysts are normalised against one another, allowing for comparative assessment across the assessed impact categories. As covered in section 7.4, the synthesis stages of forming both catalysts are identical, with only the different masses of gold (Au) and palladium (Pd) changing dependent on electrode formed.

In the context of the cradle-to-gate impacts of the CS electrodes, the dominant impacts are split between electricity use during the synthesis stages, and the constituent Au-Pd content. All other impacts combined; infrastructures, synthesis chemicals, water use, do not amount to more than ~ 5% of the total impact for any measured category. For 8 of the impact categories metal content is the dominant impact, the remaining categories are more influenced by the use of electricity. Energy is used for mixing, sonication, and drying the solution, the latter is by far the most impactful; in accordance to the consumption values shown previously in Table 7-3, page 222.

Across the majority of impact categories CS1 is more impactful due to the higher proportional mass of Au over Pd. For the Ecoinvent datasets used, Au was found to be overall more impactful than Pd on a weight-for-weight basis, the instances where CS10 come out higher (photochemical oxidant particulate matter formation, and terrestrial acidification) is down to the impact of Pd being especially impactful in these isolated categories.

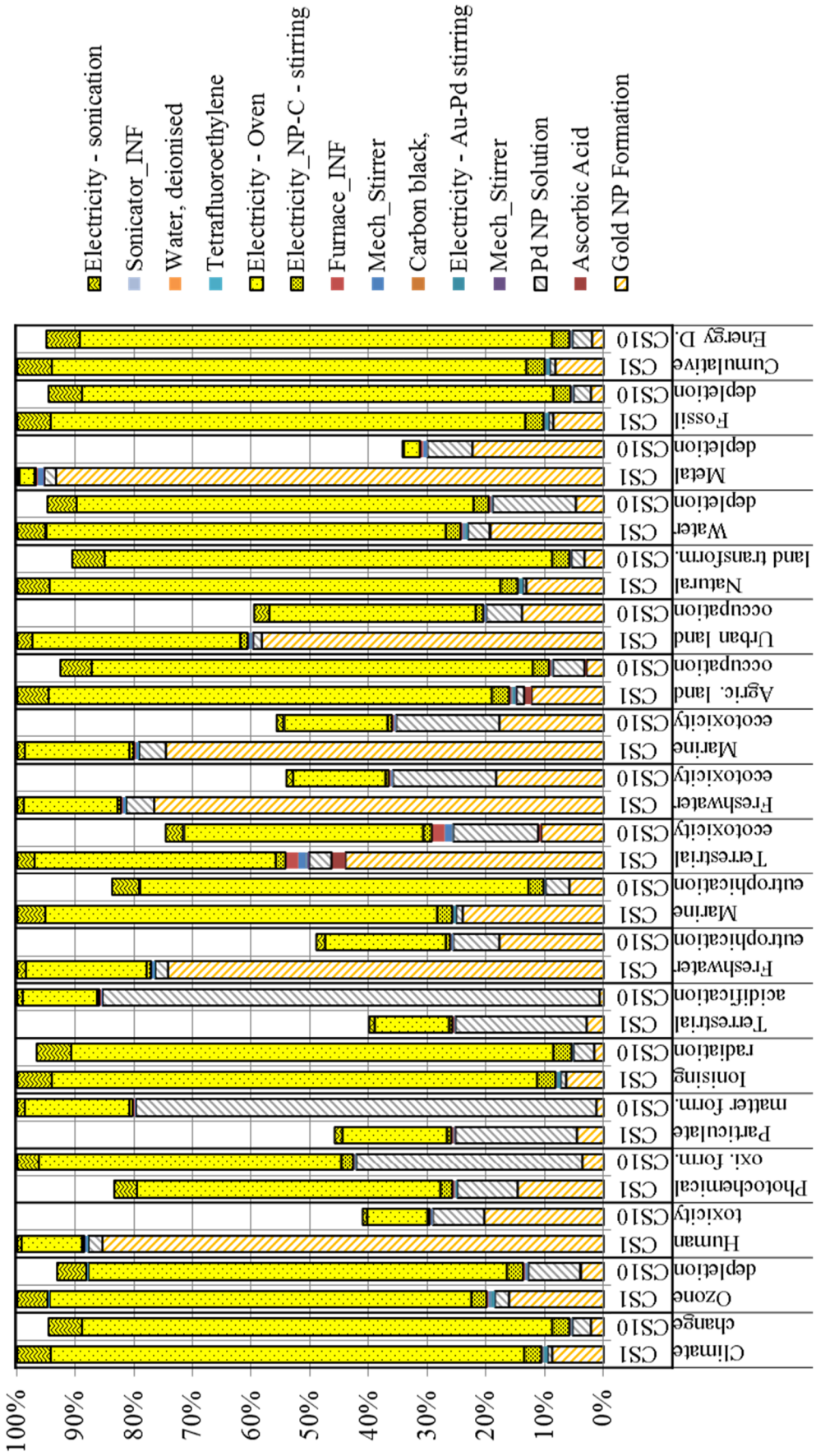


Figure 7-5 Characterised impact of final electrode coated with either CS1 or CS10

7.7.3 *IMPROVED ELECTRODE COATING IMPACTS*

This section looks at the effect of implementable measures to reduce the impacts of forming the CS electrodes, specifically:

- Reducing the highest non-metal burden of electricity usage
- Trying to recoup metals to lower the net impact of their use.

These measures include the adoption of a lean oven drying process, the recovery of used precious metals, and the adoption of renewable energy in place of current UK grid mix electricity. The resultant changes and their subsequent impact on electrode life cycle impacts are shown in Table 7-7, and discussed more fully in the following sub-sections.

7.7.3.1 Electricity reduction impacts; enhanced oven drying

Electricity usage burdens are prevalent during the electrode synthesis. The most impactful was due to oven usage, specifically its inefficient use for drying the solutes to form powders, whereby single batches would potentially be especially heated. This is an expected and understandable laboratory practice to ensure materials are heated to desired levels. However, moving towards larger scale operations offers the prospect of enhancing the oven drying process efficiency. The maximising of oven capacity - as discussed in section 0, page222 – affords enhanced material throughput thus reducing the allocation of furnace heating impact 96 times for CS1 electrode synthesis and 156 times for CS10; decided on the basis of solute to be dried and the capacity of the ovens.

Table 7-7 The cradle-to-use impacts of forming both electrodes, for the current laboratory setup and for subsequent scenarios. Scenarios are shown as a percentage of the laboratory.

	CS1					CS10				
	Lab	Lean	Lean + Renew	Lean + EOL	Lean + EOL + Renew	Lab	Lean	Lean + Renew	Lean + EOL	Lean + EOL + Renew
Climate change kg CO_2 eq	**2.6E-03**	20%	14%	40%	12%	**2.5E-03**	16%	10%	37%	8%
Ozone depletion kg CFC-11 eq	**8.2E-11**	28%	24%	41%	17%	**7.6E-11**	24%	18%	39%	14%
Human toxicity kg 1,4-DB eq	**3.9E-03**	90%	89%	45%	42%	**1.6E-03**	75%	73%	46%	38%
Photochem. oxi. form. kg NMVOC	**7.8E-06**	38%	34%	42%	21%	**9.3E-06**	48%	45%	44%	27%
Particulate matter form. kg PM10 eq	**5.0E-06**	61%	58%	48%	35%	**1.1E-05**	82%	81%	52%	46%
Ionising radiation kg U235 eq	**1.1E-03**	18%	12%	40%	11%	**1.1E-03**	15%	9%	37%	8%
Terrestrial acidification kg SO_2 eq	**2.0E-05**	68%	65%	49%	39%	**4.9E-05**	87%	86%	53%	49%
Freshwater eutroph kg P eq	**2.7E-06**	79%	78%	45%	38%	**1.3E-06**	58%	55%	44%	30%
Marine eutrophication kg N eq	**2.3E-06**	34%	29%	41%	19%	**1.9E-06**	21%	16%	38%	12%
Terrestrial ecotoxicity kg 1,4-DB eq	**8.5E-08**	57%	55%	48%	37%	**6.3E-08**	43%	39%	44%	28%
Freshwater ecotoxicity kg 1,4-DB eq	**5.4E-05**	84%	83%	45%	41%	**2.9E-05**	70%	69%	47%	38%
Marine ecotoxicity kg 1,4-DB eq	**5.2E-05**	82%	81%	45%	40%	**2.9E-05**	68%	66%	46%	37%
Agric. land occupation m^2a	**3.5E-05**	25%	20%	42%	17%	**3.2E-05**	19%	13%	38%	11%
Urban land occupation m^2a	**2.4E-05**	65%	62%	43%	32%	**1.4E-05**	41%	37%	41%	21%
Natural land transform m^2	**6.2E-07**	24%	18%	40%	13%	**5.6E-07**	16%	10%	37%	8%
Water depletion m^3	**1.8E-05**	32%	28%	42%	19%	**1.7E-05**	29%	24%	40%	16%
Metal depletion kg Fe eq	**4.8E-04**	97%	97%	47%	50%	**1.7E-04**	91%	93%	50%	59%
Fossil depletion kg oil eq	**8.4E-04**	20%	14%	39%	12%	**8.0E-04**	16%	10%	37%	8%
CED MJ	**4.8E-02**	20%	16%	40%	23%	**4.6E-02**	16%	12%	37%	20%

This ‘lean’ heating value is used in all EOL scenarios, since it is assumed that practises that reduced initial laboratory synthesis impacts would be adopted as a first step towards process improvement. The other energy consuming activities, stirring and sonicating steps, have not been modelled for a lean scenario. The reason for these omissions is because technology developers would need to verify that changes to the synthesis process do not interfere with resultant performance of formed electrodes. The final formed electrode materials are dependent on the dispersion and adhesion of metal nanoparticles with the carbon black, changing time periods and natures of these steps might incur changes in the properties/functionalities. The sonication step becomes especially prominent once the oven stage is minimised, shown later in Figure 7-7 (page 235), and thus would be the next avenue when moving towards further reduction of process impacts.

Before the exploitation of nanomaterials occurred bulk material counterparts would have been used in electrochemical cells such as gold foils (Dewulf and Bard 1988). It is likely that these materials would have been less intensive to install into the cell, than for instance a sonication step. However - informed by the LCA work conducted in this chapter - the increased impacts of incorporating nano in place of bulk materials would very likely be outweighed by the net benefit of using significantly less precious metals; since metal content for CS1 and CS10 are already such dominant impacts utilised in relatively very small quantities.

7.7.3.2 Precious metal recovery

The use of precious materials, and its subsequent loss in formed products has been identified as a major challenge for the sustainable adoption of nanotechnology (Bauer *et al.* 2008). This is again found in this LCA work, with metal usage identified as a major source of the embodied impact of forming the core shell electro-catalyst materials; LCA is well placed to measure the potential benefits in which an end-of-life (EOL) metal recovery stage could offer to mitigate the overall footprint of the materials. The approach used in this LCA work is transparent, in its accounting of the benefits of returning precious materials back into the technosphere - avoiding primary ore extraction and mining – versus the additional processes impacts that would arise from a potential recovery stage.

Figure 7-6 accounts for the benefits of an acid treatment stage, detailed in 7.6.2.2, page 220, versus the benefits of the recovered metal content for the CS1 and CS10 and the platinum counter electrode. Sonication was found to be the most impactful aspect of metal recovery, specifically the electricity consumed during this process which amounted to >99% across all impacts. An exception lies for the metal depletion category where it only accounted for 65 %; sonicator infrastructure embodied impact made up the remainder. The aqua regia (hydrochloric and nitric acid solution) accounted for <0.1% of impact during the metal recovery stage. However, this should be considered the minimum impact of the potential process, since the quantity used is based on the stoichiometric amount for metal dissolution not accounting for any losses or extra for subsequent washing etc.

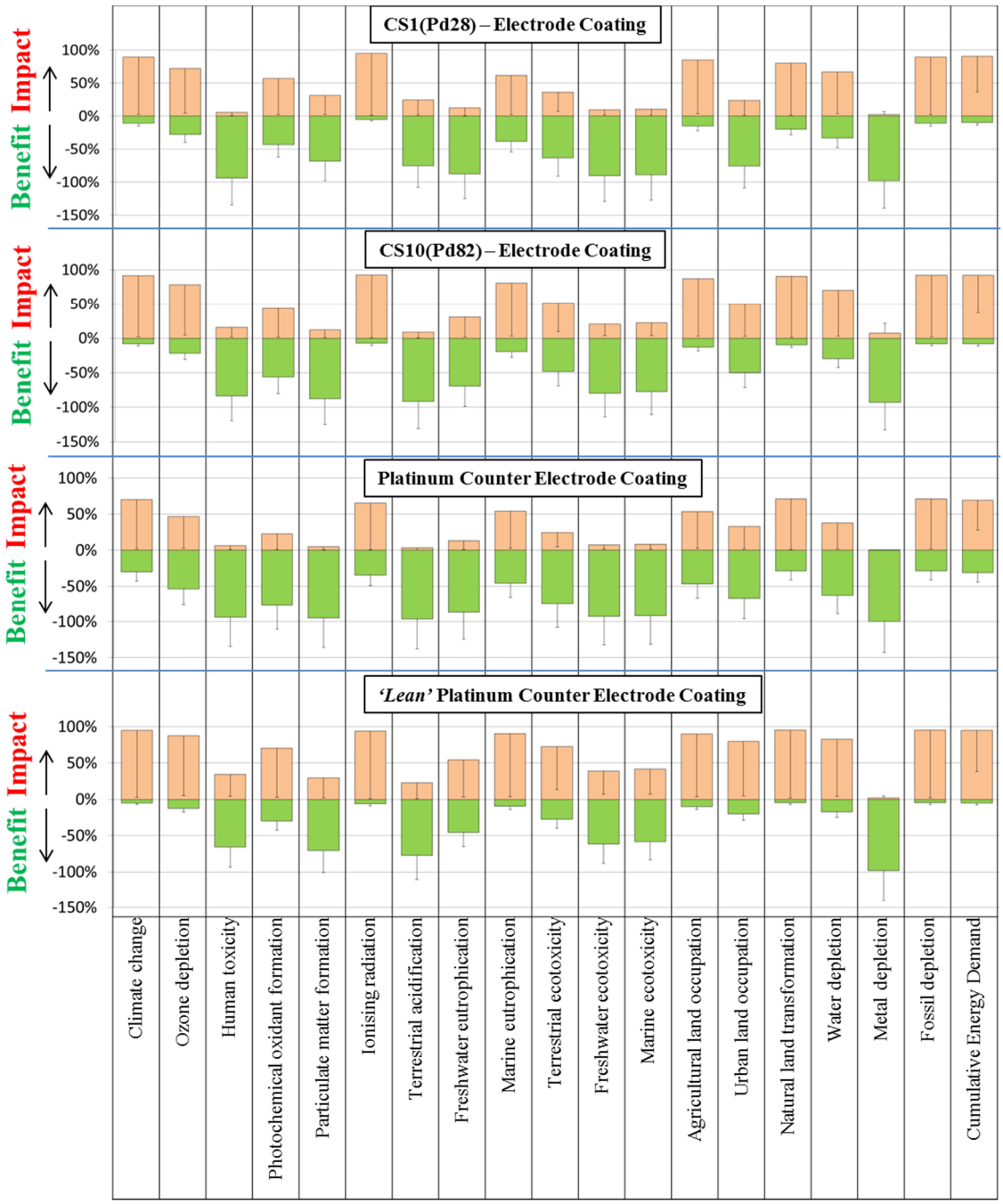


Figure 7-6 End of life impacts (orange) versus the benefits of retrieved catalyst precious metals (green).

Error bar shows change in impact should renewable electricity be used, and if 100% of deposited metal could be retrieved, respectively.

In Figure 7-6 it can be seen that there are pros and cons of the acid treatment recovery of the precious metals. Metal depletion impacts are understandably improved along with toxicity and eutrophication categories. However, the GWP, fossil fuel use and CED impact - amongst others - are all worsened by the introduction energy intensive sonication stage. This is an important consideration that accompanies the use of such materials. The process of metal recovery might well improve with a tested and refined treatment stage, however, a trade-off between renewable benefit and resulting additional impact will always likely have to be considered.

The use of a renewable wind power source in place of UK electricity grid mix would lower the burdens of the acid treatment stage, this is shown as whiskers (a.k.a error lines) on the respective 'impact sides' of Figure 7-6. Renewable exploitation leads to improvements for all impacts apart from metal depletion, where wind use is more intensive per unit electricity obtained (see chapter 3). Similarly the maximum beneficial range of improving the treatment stage to achieve 100% recovery, is shown as outlying whiskers on the 'benefit side'.

7.7.3.3 Resultant improved electrode impact

The effects of the lean - or improved efficiency - synthesis heating process, and the introduction of an end-of-life (EOL) metal recovery via an acid treatment stage is shown for the CS1 electrode in Figure 7-7; where the current laboratory process is compared against the 'lean + EOL' model.

Overall the impacts show that the formed electrode would be between 39 and 47 % of the current laboratory setup. Metal impacts are seen to be lowered due to the ability to recoup materials, although the introduction of the acid treatment stage as an additional activity proves to be one of the most dominant life cycle activities associated with material impacts.

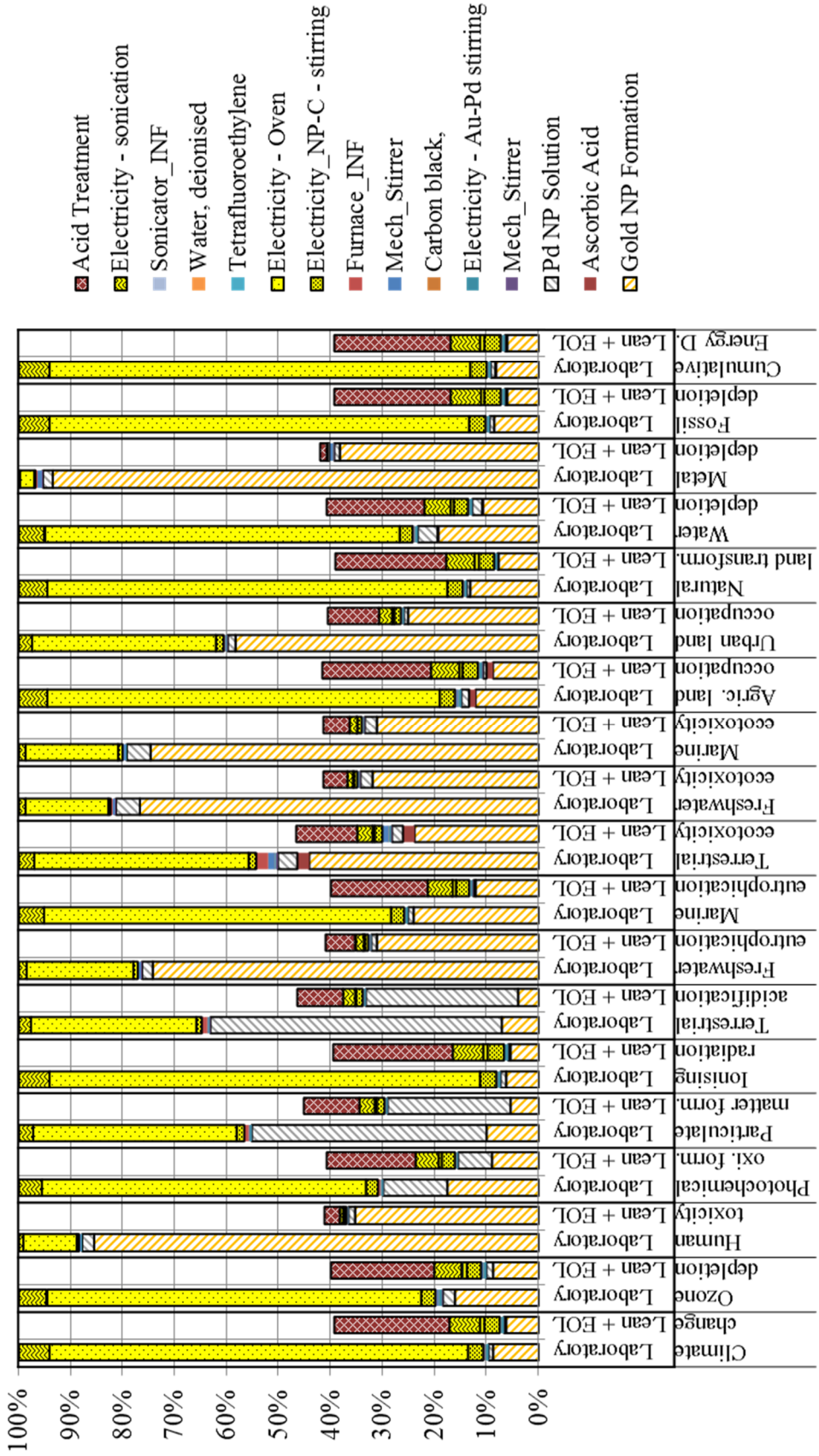


Figure 7-7 CS1 electrode coating, comparison between lab synthesis and lean+EOL+renew

More verification work will be necessary to validate the EOL processing stage, since at present it is a theoretical estimation of a likely route. However, the EOL recovery of ENMs has already been established to be a high-burden activity for nanomaterials, with lower concentrations of material and changed properties from bulk counterparts increasing the intensity of retrieval activities (Olapiriyakul and Caudill 2009).

7.7.4 *INFRASTRUCTURE COMPONENT RECYCLING*

For the used infrastructure equipment, the constituent metal, glass, and retrievable plastic components are modelled as retrievable materials. The actual mechanisms for material retrieval has been omitted due to uncertainties over this stage, in defence of this omission Hischier *et al.* (2005b) investigated the impacts of a European electronic equipment take-back and recycling system, and concluded the efforts for material recovery offset the invested effort significantly. The end waste flows are negated in this study. Very little non-recyclable material wastage is assumed, and the ratios of material quantity in comparison to the system flows are very small.

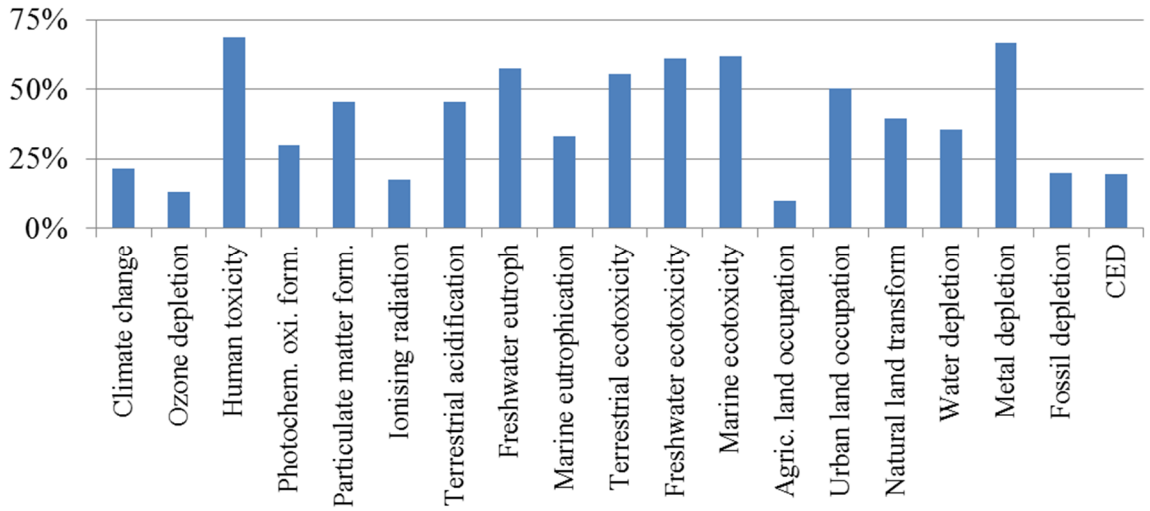


Figure 7-8 Potential benefit from recoverable content of potentiostat

The work of Hischier *et al.* (2005b) conduct LCAs on the retrieval of primary materials from a suite of electronic devices; which found significant benefits to the recovery and re-introduction of recyclable materials into the supply chain. That study considered the electronics waste directive of Switzerland, which is broadly in-line with other EU directives such as the Waste Electrical and Electronic Equipment (WEEE). For this work the physical waste recovery stages have not been modelled in great detail, due to uncertainty of the final electrochemical cell design and indeed uncertainties of the

recovery route likely to be adopted. However, the transport and extraction activities are likely to be minor percentile values in terms of the returned benefits of material recovery (Hischier *et al.* 2005b)

Considering the impacts of the operating potentiostat, i.e. broadly the sole infrastructure controlling and powering the cell operation, Figure 7-8 compares the embodied impact of the modelled potentiostat (Rowe *et al.* 2011) to the amount of recoverable benefit prevalent in the form of reusable metals and glass components. Recycling of major components would result in an upper-bound recovery of 10 – 70% of the initial infrastructure impact. Discrepancies between the impact and recovery benefit are primarily down to:

- Emissions released during primary material production and assembly,
- Inability to recoup flows such as chemicals and energy involved in the production,
- Unrecoverable elements such as thermoset plastics, resins, material coatings etc.

7.8 OPERATIONAL SCENARIO ANALYSIS: LABORATORY AND MOVING FORWARDS

7.8.1 *ASSUMPTIONS AND METHODOLOGY*

The synthesis formation impacts of the CS electrode coatings have been previously discussed, along with scenarios for improved environmental impact through enhanced heating efficiency and recovery of precious metals. Similarly, the impact of the operating cell has also been explored, the major assumptions for the different modelled cases are shown in Table 7-8, overleaf.

Much of the LCA model has been provided for a 'leaner' setup than the laboratory worst-case. For example, the electrode substrate of graphite is considered for smallest possible allocation for the amount needed for ink coating, and superfluous activities such as heated air-drying of electrode surfaces are ignored. Furthermore, the use of the equipment based on time-allocation rather than laboratory practise dictation, e.g. a device used for 1 hour is imprinting 1/(8760 × lifetime) impacts onto the flow passing

through it. The model has been constructed in this way to provide the most relevant and meaningful account of the operating system.

Table 7-8 The scenarios used in the assessment of the electrochemical process

	Electrode	Infrastructure
Laboratory	**Modelling of current synthesis procedure.**	**Laboratory setup, using one potentiostat per operating cell.**
	Allocation of all equipment usage is already akin to a 'lean' setup, i.e. based on time duration of activity based on total lifetime of the equipment.	
Lean	**Reduced oven usage for CS1 and CS10 electrode synthesis, section 7.7.3.1.** **Reduction of 85% platinum content in counter electrode, section 7.6.3.1.**	**Allocation of potentiostat based on provision of deliverable electrode current, section 7.6.3.2.**
Lean + End-of-life	**Same as lean with recovery of metal content of electrodes 0**	**Recycling of major infrastructure components, section 7.7.4.**
Lean + End-of-life + Renewable Electricity	**Same as lean + end-of-life, but with use of renewable source for activities requiring electricity.**	**Operation of cell occurs with a renewable source of electricity.**

The most prevalent findings of the LCA work are summarised in the following sections. The LCA results are presented in a manner to allow one to ascertain where laboratory material and energetic inefficiencies could be mitigated, and likely further technical changes that would require addressing before the assessed electrochemical conversion routes become environmentally favourable pathways to pursue; in terms of forming products and climate change mitigation through CO_2 conversion and utilisation.

7.8.2 *OPERATIONAL LIFETIME ASSUMPTIONS*

When assessing the operation of the electrochemical cell, an assumption was taken that the major infrastructure could operate for 30 years without major componentry changes. The catalyst lifetime was modelled to last 5000 hours, a figure to allow cross-comparison with the results of the RWGS-FT process (Chapter 6).

At present the operation of an electrochemical cell at the durations hypothesised in this LCA have not been physically achieved, indeed some researchers – albeit for copper-

based cells - report marked electrochemical performance reductions after a few hours usage (Li and Oloman 2005). It must be noted however, that the electrode materials CS1 and CS10 have shown no measurable evidence of catalytic 'drop-off' over two hour run times. The deficit between a few hours and operations of months, years, or more is considerable further research is required to establish achievable catalyst lifetimes. In addition catalyst re-activation stages will require development and consideration in the context of the process life cycle.

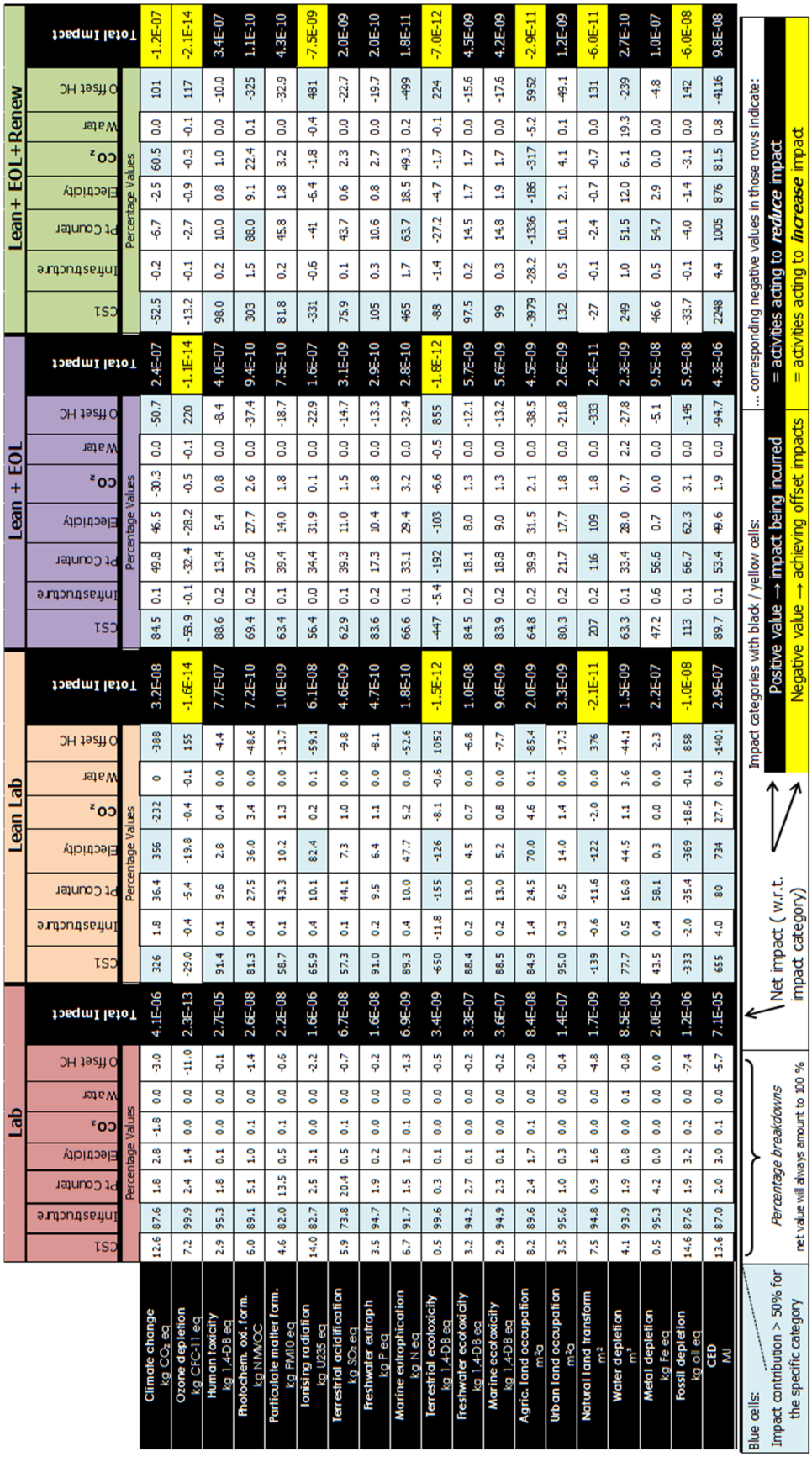
Sustained catalyst performance is a major hurdle if a feasible operable electrochemical process is to be developed for CO_2 reduction. The LCA results will dictate targets for catalyst lifetime to be met in order for the process to prove environmentally favourable.

7.8.3 *ELECTROCHEMICAL CELL OPERATIONAL LCIA RESULTS*

Life cycle impact assessment results have been disseminated for the embodied impacts of the electrochemical cell, and the in-use flows / operation of this cell. These results are presented for (in the interest of space and fluidity) the best performing catalyst electrode, i.e. CS1 alone. Table 7-9 provides the results of operating an electrochemical cell: with CS1 electrode coating, across the scenarios outlined in Table 7-8, and for the assumed lifetime of the coatings and operating infrastructure.

For the laboratory process no net offset is achieved for any impact category, i.e. the per hour operation of the cell is more impactful than the GHG benefit of locking away the CO_2 from the atmosphere. Furthermore, and including wider environmental impact categories, the electrochemical process of producing the chemical products is much more impactful than existing routes. Much of the burden at laboratory scale is due to the infrastructure, i.e. potentiostat, which proves to be the domineering impact; 73.7 to 99.9% dependent on category.

Table 7-9 CS1 catalyst per hour impact for the four modelled scenarios. Process assumption: catalyst operational lifetime = 5000 hours, infrastructure = 30 years.



The lean setup provides two notable changes, infrastructure now a minor rather than major impact, and environmental offsets are achieved for four impact categories. The lean+EOL scenario brings with it expected findings with regard to some impacts showing favourable and others unfavourable changes over the lean scenario. This can be appreciated since at the lean scale the electrode coating impact is broadly the most dominant contributor, and thus -in accordance to the findings of 7.7.3.2, page 232– the benefit of retrieving the gold-palladium content of the electrodes depends on specific environmental impacts.

Once renewable energy is considered to accompany the other enhanced process changes, the process meets net-negative GHG operating conditions, along with 6 other net-negative environmental impacts. This therefore indicates that there is a benefit from the perspective of carbon capture and utilisation for operating this process, providing the lean adaptation, metal recovery and use of a low-carbon electricity source can be achieved.

The accompanying appendix details data for CS10 impacts, however, the operation of both catalysts show similar trends. The operation of CS10 has the same operating impacts, and thus as a consequence to a lower CO_2 conversion, less beneficial offsets are seen; thus total impacts are higher and less environmentally favourable conditions are met.

7.8.4 *OBTAINING GHG NEGATIVE IMPACTS*

A better visualisation of CCU performance and wider environmental benefit is shown in Figure 7-9; providing a breakdown of the operation of the CS1 electrode (over a prescribed 5000 hour catalyst, and 30 year infrastructure respective operational lifetimes), using either the UK grid or a renewable wind electricity mix; i.e. as shown for ‘Lean + EOL’ and ‘Lean+EOL+Renew’ in Table 7-9. Impact bars which cross the -50% line indicate that the majority of operational impacts are negative, and thus favourable environmental offsets are met in these cases.

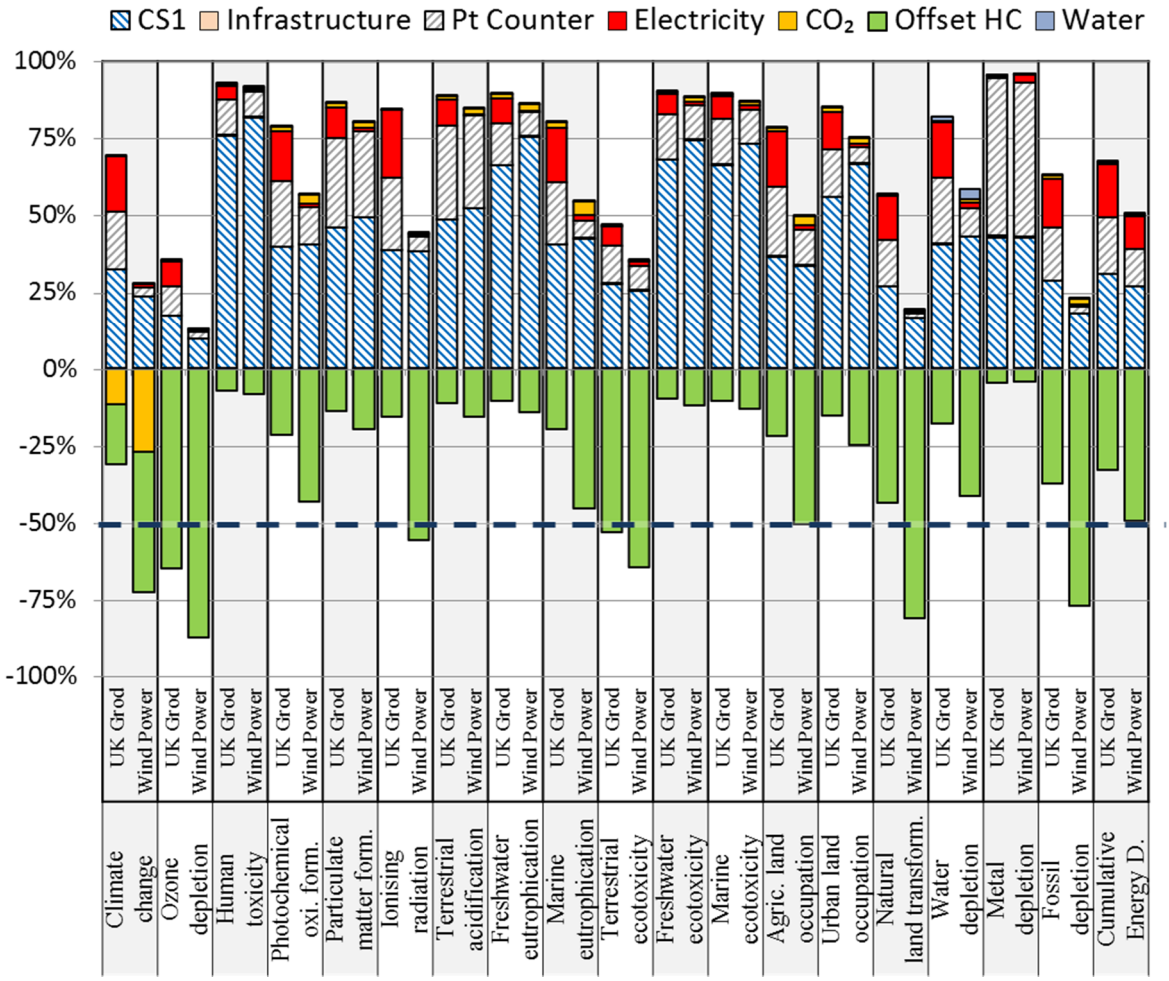


Figure 7-9 Lean+ EOL, with with either UK grid or renewable electricity

Considering the case for net negative carbon footprint, independent of product formed, i.e. ignoring the offset achieved by producing chemicals void of their production pathway. The best case modelled comes very near to achieving this CCU goal with the CO_2 immobilised offsetting 98% of the operational impact of the CS1 cell, for the UK grid this figure drops significantly to only 17%.

The ability to achieve neutral/negative impacts can be seen to be very dependent on the electricity source used, only ozone depletion and terrestrial ecotoxicity impacts are being offset rather than incurred when the UK grid mix is being used. All other impact categories, to varying degrees, can be considered some way off meeting environmentally neutral/negative impacts. When considering the operation with UK grid electricity, process improvements alone would unlikely meet the impact deficit(s), since CS1 has a faradaic efficiency of 92% affording little margin for increasing hydrocarbon yield / decreasing energy consumption. Additionally the reduction of

embodied CS1 and Pt counter embodied impacts would need substantial minimisation past 70% retrieval.

The use of renewable wind electricity can be seen to provide a means of sequestering CO_2 while providing GHG negative impacts; here, the immobilised CO_2 and offset hydrocarbons outweighing the burden of the operating cell. In addition to meeting favourable carbon capture and utilisation (CCU) performance, six other impact categories display net negative results when renewable wind power is used to operate the cells and be part of the electrode synthesis stages. CED is only marginally from being net-negative, and other impacts are very close to net negative offset; appreciably within a margin whereby, e.g. slight increase metal recovery improvements would allow the conditions to be met.

Therefore, from this early scoping assessment it would seem likely that the use of renewable electricity, or at least lower impact source than the current UK grid, is required for favourable environmental performances to be met. However, as shown in Figure 7-9, it seems likely that some impacts will always be incurred when operating the electrochemical process. Decision makers will have to decide whether these are acceptable penalties.

7.8.5 *IMPACTS OF PRODUCTS FORMED*

The process for accounting for product impacts is in alignment with the approach laid out in chapter 3 specifically section 3.8.2, (page 64). Covered in greater detail in the heterogeneous CO_2 conversion chapter 6, section 6.13 (page 201). Table 7-10 compares the impact of forming the likely products via the electro-catalytic route instead of existing production processes. In brief, values less than 1 indicates a lower burden product being produced. With the assumed product yield of 1/3 formic acid, methanol, and carbon monoxide respectively, it can be seen that for the lowest impact operating electrochemical cell that impacts as low as 25% in comparison to existing routes can be achievable. However, no net negative impact values are shown, meaning that the production of the chemicals in themselves are not carbon sinks, but can allow for carbon offsets in the context of comparable product life cycle.

Table 7-10 Impact of forming products via the electrochemical routes assessed in comparison to existing routes.

Cell colour key:	>100 times impact
	<100 times impact but >1 0
	< 10 times impact but >1
	Less impactful

	CS1	CS10
Laboratory	690	694
Lean	25.3	29.2
Lean + Renew	2.03	4.19
Lean + EOL	59.8	64.3
Lean + Renew + R-EOL	0.25	3.04

7.8.6 *REQUIRED OPERATIONAL LIFETIME TO MEET ENVIRONMENTAL TARGETS*

The previous sections set prescribed lifetimes to allow for cross-comparison between scenarios. For the 5000 hour catalyst lifetime, 30 years for infrastructure, where favourable conditions, as stated, were met for some of the impact categories. To gain a better understanding of the feasibility of the processes, the temporal measure of environmental 'break-even points' was considered. In essence, the 19 assessed environmental impacts are measured in terms of the duration of time a catalyst/infrastructure would have to operate before favourable environmental conditions are met.

The break-even point is assessed in a disaggregate form, with the catalyst lifetime determined in isolation from the catalyst with infrastructure (whole system boundary); when referring to 'catalyst' this includes the CS and counter platinum electrode impacts. This from the perspective of technology development allows focus to be steered on material and/or process enhancement. The break-even points, in terms of years, are presented in Table 7-11. Black cells within the table indicate impacts, for any operating length, will never be counteracted by the embodied and fugitive emissions associated with the operating electrochemical cell. For catalyst CS1, it can be seen that ionisation radiation, terrestrial acidification, marine eutrophication and water depletion are not offset until the 'best' case model – using renewable electricity - is considered.

Table 7-11 Break-even point, or minimum lifetime (in years) for; catalyst (Cat) ignoring infrastructure, or catalyst with infrastructure (Cat + Inf), before environmental benefits are achieved from the operating process.

	Lab		Lean		L + EOL		L+E+Ren	
	Cat	Cat + Inf	Cat	Cat + Inf	Cat	Cat + Inf	Cat	Cat + Inf
Climate change	4.0	1291	0.8	1.0	2.2	2.3	0.21	0.24
Ozone depletion	0.58	315	0.1	0.2	0.3	0.3	0.08	0.10
Human toxicity	84	89105	51	55	27	30	7.47	8.32
Photochem. oxi. form.	24	10277	6.7	8.1	8.6	9.3	0.76	0.92
Particulate matter form.	103	24647	27	29	20	21	2.62	2.84
Ionising radiation							0.45	0.49
Terrestrial acidification							3.46	3.62
Freshwater eutroph	165	153372	93	102	57	63	4.11	4.59
Marine eutrophication							0.70	0.82
Terrestrial ecotoxicity	1.1	7443	0.50	0.89	0.49	0.71	0.30	0.50
Freshwater ecotoxicity	69	58065	36	39	21	23	5.23	5.79
Marine ecotoxicity	65	62483	34	37	20	22	4.65	5.21
Agric. land occupation	23	10396	5.76	9.52	12	13	0.56	0.71
Urban land occupation	60	67626	32	37	26	28	1.90	2.22
Natural land transform	1.5	891	0.34	0.41	0.83	0.86	0.13	0.15
Water depletion							0.85	1.00
Metal depletion	128	135393	30.0	35.8	14	17	31.2	39.6
Fossil depletion	2.3	649	0.45	0.58	1.3	1.3	0.16	0.19
Cumulative Energy	3.4	1009	0.66	0.85	1.9	2.0	0.59	0.63

Key; payback period:	< 1 year	> 1 but < 10	>10 but < 50	> 50 years	**Never**

For impacts that can be offset, i.e. non-black cells, the move from a laboratory to a 'lean' setup dramatically reduces the respective payback periods. The current laboratory setup - of one potentiostat per operating cell - would need to operate thousands of years to be environmentally neutral! Catalyst impacts considered in isolation at the laboratory scale have much better payback periods, especially for a 4.7 year payback for climate change. However, even for a catalyst void of infrastructure at the laboratory scale, there would still be the need for its lifetime to span many decades before the majority of other environmental burdens could be offset. The difference between lean, and lean with end-of-life metal recovery, is again dependent on impact category and follow similar trends as previously discussed.

A low payback period is due to a combination of factors, predominantly due to a smaller deficit between the life cycle impacts of forming a chemical via the electrochemical route versus the impact of forming the same chemical via existing production process (covered in 7.7.1, page 227). Impacts which never payback can be considered occasions where the electrochemical process operation is more impactful than the achieved offsets of chemical production. The final case of utilising renewable wind along with the other process improvements appreciably leads to the process having reasonable paybacks across the impact categories; the vast majority -considering catalyst with and without infrastructure- payback within a year.

An exception to 'reasonable' paybacks is seen for metal depletion, where operation of 31 – 40 years would be needed. This is exacerbated with the use of the renewable wind dataset, indicative of when the adoption of processes with conflicting environmental benefits/penalties must be weighed up for the best overall sought solution. Improvements in the metal recovery stage, to provide recovery rates of metal greater than 70%, would result in direct and significant effects in minimising the longer payback periods, and as such would be an immediate area of focus when developing the process to larger scales.

Metal depletion impacts are a collective term for metals taken from ores in the ground; normalised against the abundance of these metals in comparison to the reference metric of iron ore. This impact can be considered especially hard to minimise since the

traditional routes of carbon monoxide, formic acid and methanol do not use concentrated quantities of precious metals- appreciably very high impact extraction- in their synthesis. This makes the recovery of precious metals all the more essential if the process is to attempt to be environmentally competitive as a potential pathway.

7.8.7 *IMPACTS OF CONVERTING A KILOGRAM OF CO_2*

Table 7-12 Resultant impact of converting one kilogram of CO_2, for the lean + eol + renewable operating case.

	CS1	CS10
Climate change kg CO_2 eq	-1.3	-1.1
Ozone depletion kg CFC-11 eq	-2.3E-7	-2.0E-7
Human toxicity kg 1,4-DB eq	3.7	3.5
Photochemical oxidant form. kg NMVOC	1.2E-3	1.0E-2
Particulate matter formation kg PM10 eq	4.7E-3	2.7E-2
Ionising radiation kg U235 eq	-8.3E-2	9.1E-2
Terrestrial acidification kg SO_2 eq	2.2E-2	1.3E-1
Freshwater eutrophication kg P eq	2.2E-3	2.1E-3
Marine eutrophication kg N eq	2.0E-4	4.5E-4
Terrestrial ecotoxicity kg 1,4-DB eq	-7.7E-5	-3.2E-5
Freshwater ecotoxicity kg 1,4-DB eq	4.9E-2	6.3E-2
Marine ecotoxicity kg 1,4-DB eq	4.6E-2	6.1E-2
Agric. land occupation m^2a	-3.2E-4	9.6E-3
Urban land occupation m^2a	1.3E-2	1.2E-2
Natural land transform m^2	-6.6E-4	-6.1E-4
Water depletion m^3	3.0E-3	1.4E-2
Metal depletion kg Fe eq	1.1	1.8
Fossil depletion kg oil eq	-6.6E-1	-7.0E-1
Cumulative Energy Demand MJ	1.1	38.0

The impacts of converting one kilogram of CO_2 feedstock are stated in Table 7-12, these values are for the modelled scenario where net-negative climate change values are witnessed, i.e. lean setup, with end-of-life metal recovery and use of renewable wind dataset. At these conditions the operation of CS1 converts every unit of CO_2 into 1.3 times (1.1 for CS10) as much CO_2 equivalent avoided emissions. These impacts remain

true if the electrochemical process were to be scaled from the existing modelled setup; maintaining the same functional performance.

At the current laboratory scale, the CS1 cell is converting 90 nanograms ($x10^{-9}$) per hour of CO_2, if a more modest 'one kilogram of CO_2 per hour' were to be sought, the process would need to operate at a scale of ~11 million times larger than the current process. This scale-up would translate to the use of ~70 g of gold, and 20 g of palladium respectively, and consuming 139 kWh.

7.8.8 *A NOTE ON FEASIBILITY OF ELECTROCHEMICAL PROCESS SCALE-UP*

The cell investigated can be considered as a fuel cell working in reverse, or an electrolyser, whereby an electrical current is applied to it resulting in an internal chemical change. Both fuel cell and electrolyser (unlike batteries) are 'recharged' by the replacement of the cell reactants. The physical construction of both devices are identical, the specific catalysts and reactants used are the determining factors for the products / energy generated. Pehnt (2001) conducted an LCA on a hydrogen fuel cell stack detailing the cradle to gate production impacts of the device. Major findings from Pehnt's LCA were that the platinum group metals were predominantly the largest source of impacts, followed by the high energy intensity of catalyst integration of catalyst within the graphite plates of the cell, and to a lesser extent the the ion-exchange PTFE membrane. Pehnt's study findings are analogous to the major findings of this thesis chapter, providing confirmation that when considering the development from laboratory to larger / pilot-scale devices, the major sources of impacts remain very similar. Given the nature of the process, it is unlikely that significant shifts in relative environmental contributors would occur even at significantly larger scales.

Electrochemistry, more specifically an electrochemical cell is, arguably, modular or scalable in its nature. The cell assessed could, in theory, be connected in series with other cells, converting larger volumes of CO_2, and forming more products, for a proportional increase in electrical power and process reactants. In terms of catalytic material usage, the nanocatalysts are approaching the maximum surface area per mass of metal use, maximising the electro-catalytic performance. Therefore, no enhanced efficiency through the roll-out of larger technology scales is expected. Thus the retrieval

of precious materials, and energy efficiency enhancements are most likely to be the area where the environmental gains could be achived.

A master's thesis was found during the course of this research (Robledo-Diez 2012), which conducted a life cycle energy assessment of a pilot-scale electrochemical route of formic acid, HCOOH, production. Although not detailing the nature of the catalysts used, the proprietary data provided by an industrial research collaborator, provided an insight into the energetic process stages of a more established 100 ton / day capacity plant. The study had coverage of the downstream processes i.e. the subsequent separation and distillation of products after leaving the electrochemical cell. These additional stages, (not modelled due to absence of data an uncertainty over potential pathways) were stated to account for approximately 20% of the total energy requirements; with reference to the findings of the LCA work of this thesis chapter the inclusion of these additional stages would offer minimal changes to the overall findings. However, the follow-on work would appreciably be required and a future expansion of scope to cover additional activities.

Considering the approach and coverage of this LCA work, the results can be deemed valid in capturing the major impacts of electrochemical conversion of CO_2 into carbonaceous products.

7.8.9 *NANO-SPECIFIC IMPACTS*

The general properties of the engineered nanomaterials (ENM) of this work are detailed in Table 7-1, page 216, more information including electron microscopy images are available in Celorrio *et al.* (2012b). In summary carbon black in size ranges of 30 to 60 nanometres, have impregnated with gold-palladium core shells, with particle sizes in turn of between 20 and 40 nm.

The damaging effect of carbon black on the respiratory system has been known for many decades, with exposure linked with health effects such as increased rate of asthma (Gardiner *et al.* 2001). The addition of NP metal is unknown in terms of any additional respiratory effect. The effect of palladium is discussed in chapter 5. Additionally, nanogold carries health concerns and unlike bulk unreactive counterpart exhibits increased reactivity - hence its growing nanotechnology applications. Studies

have shown effects on aquatic organisms with cellular and genetic damage (Asharani *et al.* 2010) and that inhaled gold particles can not only cause cell damage at this interface, accumulating over time, but translocate via cellular uptake and effect other organs within a mammalian body(Yu *et al.* 2007). However, despite recognised health risks there is yet to be any conclusive metrics to assess the risks of nano gold due to the many uncertainties still present (Lévy *et al.* 2010).

The release points across the life cycle are expected to be largely limited and mitigated against. During the synthesis, the wet synthesis techniques act to prevent particles becoming airborne, and is handled in this way until deposition and subsequent drying on the electrode surface, the nafion solution adheres the particles firmly in place. In the event of particle degradation during use the particles might potentially break free and enter the electrolyte solution, however, this is again within an aqueous environment within a closed system.

The only identifiable point of ENM exposure is during the dry powder phase, appreciably occurring between the oven heating and dispersion in nafion, see Figure 7-1 (page 215). During this point fine particles may potentially be a hazard, consequently, they are handled with this in mind during laboratory fume hood operation etc.

7.9 ELECTROCHEMISTRY CONCLUSIONS

This chapter has captured the environmental implications of a novel electrode material capable of converting CO_2 into valuable small-chained molecules; CO, HCOOH, CH_3OH.

7.9.1 *CRADLE-TO-GATE OF THE FORMATION ROUTES OF DIFFERENT ELECTRODES*

Two electrode coatings were investigated, each with different relative loadings of palladium nano-width shells encasing gold nano-cores. The final impacts of the formed catalysts are heavily dominated by the mass of deposited nanoparticulate metals present, particularly the more impactful gold content, thus the heavier gold-loaded CS1 catalyst was, on balance, more impactful than an equivalent electrode coating of CS10.

The process energy usage during the synthesis of the electrodes was a major environmental impact, dependent on impact category this would often outweigh the impacts of the precious metal usage. The adoption of a more efficient heating stage, i.e. moving from laboratory to a more continuous synthesis process, significantly minimised the impact of energy. The retrieval of precious metal via an acid treatment stage acted to reduce the impacts where metal usage were dominant. This metal recovery stage increased the impacts of where electricity was more impactful, since the modelled acid treatment is an energy intensive activity.

A switch from a current UK electricity mix to a renewable wind source, saw a significant reduction in the final impact of the formed electrode coatings. Finally, the impacts of equipment infrastructure and other upstream chemical reactants and materials were found to be of negligible concern.

7.9.2 *ENVIRONMENTAL IMPACTS AND IMPLICATIONS OF RESULTANT PRODUCTS FORMED*

At the time of conducting this LCA the exact mix, or indeed presence, of the modelled CO, HCOOH, and CH_3OH production has not been established, therefore a mean estimate of equal conversion to the three likely products was performed in the assessment. Hydrogen is a proven and measured product from the cell, formed from the reduction of water within the cell; the presence of hydrogen formation has been used to infer the other carbonaceous products being formed. Dependent on the scenario modelled, as will be elaborated further shortly, it is feasible for an electrochemical process based on the assessed laboratory chemical performances, could produce products at a lower environmental 'cost' than traditional existing industrial routes.

From a fundamental starting point, considering only the transformation of carbon-captured CO_2 into any CO/HCOOH/CH_3OH product displays a net beneficial environmental footprint. The impacts of the captured CO_2 is outweighed by the avoided impacts of not sourcing CO/HCOOH/CH_3OH from existent industrial sources. This does not, however, consider the life cycle impacts of the operating electrochemical process; electrodes and other cell constituents, cell electricity consumption, and other associated chemical and material flows.

When a full life cycle is considered, as shown in the system boundary of Figure 7-1, then the electrochemical process in its current guise is not an environmentally favourable option across any measured impact category. The predominant reasons for the process shortcomings are:

I. UK electricity grid mix

II. Electrode working life time

III. Products are not 'paying back' the unique burdens associated with the electrochemical process, mainly precious metal usage

An expansion of the assessed system boundary was made to cover theoretical, yet implementable, process changes. These changes included a more lean synthesis of electrode production and operation within the cell, and an end-of-life metal recovery of deposited precious metals. The introduction of these measures significantly lowered the majority of 'break-even' points, subsequently reducing the working lifetime criterion of the electrode coating, and more importantly lowering the resultant embodied impact imparted on the formed products. In the best case, the impacts of products were 25% compared to reference chemical production routes.

Uncertainty over exact product mixes formed prevents more quantitative remarks with regard to specific products formed, however, with such a low / impact negative GHG operation it is likely that the resultant products formed will be significantly less impactful than their counterparts formed in traditional industrial processes.

7.9.3 *PROCESS PERFORMANCE AND INHERENT IMPACTS*

From the perspective of a carbon capture and utilisation (CCU) process, the electrochemical route assessed has the potential to be a carbon offset when used with a renewable electricity generator, offsetting more GHG emissions than its life cycle activities generate. In the best case the process of converting one kilogram of CO_2 results in 1.3 kilograms of offset greenhouse gas (GHG) (CO_2 equivalent) emissions. Contributing to this value was the inclusion of avoided offsets of the formed products, however, the process itself approaching operational carbon neutrality with the immobilisation of CO_2 to the atmosphere offsetting 98% (i.e. nearly surpassing 100% and

becoming a carbon sink) of the process operational impacts. In the same best case models when renewable energy is not used, and the UK grid is modelled to power the cell, this figure drops significantly to only 17% of operational impacts being offset.

For the case of 5000 hour catalyst, and 30 year infrastructure operational lifetimes, global warming in addition to six other measured impacts could be offset. However, the remaining 12 categories would be incurring impacts.

When seeking to determine the process operational lifetimes that would need to be achieved before favourable environmental impacts are met across all categories (with reference to Table 7-11, page 245). It was found that all in addition to climate change impacts, 15 out of 19 other impacts are theoretically offset for the cases using UK grid electricity, however a large proportion of these offsets require electrochemical cell operation for a decade or more. When using renewable wind source all impacts can be potentially offset within 5 operating years; with the exception of metal depletion which would require 30 years or more of operation, and 8 years for human toxicity impact offset.

The assessed electrochemical process, modelled *via* the LCA, and its associated assumptions, always shows metal depletion burdens as, arguably, unrecoverable inherent impact. The use of palladium-gold at the working electrode, and a platinum counter electrode ensure the cradle-gate-impacts are, for the system assessed, too great an initial environmental hurdle to be overcome in this metal depletion category.

7.9.4 *IMPLEMENTABLE PROCESS IMPROVEMENTS*

Much of the scenarios assessed have displayed that significant improvements, often impact nullifying outcomes, are achieved through the adoption of:

- Renewable / low impact electricity sources.
- Working electrode coatings that can last at least 6 months to see environmentally favourable operations for the majority of assessed impact categories.
- End-of-life metal recovery from catalysts, and major constituent material recycling from the equipment infrastructure.

Further, and significant, improvements would be seen if metal recovery rates could be shown to exceed the 70% approximation modelled in this LCA.

The LCA work has captured the majority of key working components, and is in agreement with results for fuel cell impacts (Pehnt 2001), however a better appreciation of the final operating electrochemical cell would allow a more accurate account of the working process infrastructure embodied impacts.

At present, electrochemical catalysts are not proven to last for the durations necessary for the respective life cycle burdens to be counteracted, this LCA work is therefore instructive for developmental targets. Fellow investigators and others following the methodology laid out in this chapter for this electrochemical process will see catalyst lifetime and sustained catalytic performance as a priority for the feasibility of this CO_2 utilisation route. The LCA can be considered scalable in relation to products formed and CO_2 converted, with an acceptable range of accuracy.

Chapter 8: KEY FINDINGS AND DISCUSSION

This chapter presents the major findings from the distinct yet interlinked studies contained within this thesis. More specific and detailed discussion points are contained within the relevant chapters. However, the key findings and comparison between technologies are presented, with a specific focus on the dominant factors behind the findings, and identified areas of improvement for the methodologies used.

8.1 FINDINGS FOR THE NANOMATERIALS INVESTIGATED

This thesis looked at three specific ENM types, and different variations within these:

- Multi-walled carbon nanotubes (MWCNT), grown via chemical vapour deposition (CVD); prepared for catalysis application via iron activated Fe@CNT, or iron-decorated Fe_Dec_CNT. Covered in chapter 4, and related collaborator publication O'Byrne et al. (2013).

- Iron and iron-palladium nanoparticles deposited via a wet deposition technique onto micro-porous silica supports; these materials are annotated as FeXPdY-SiO2, relative to the SiO2 substrate mass: X varies between 10 and 40 wt.%, and Y 1 to 4 wt.%, respectively. Covered in chapter 5, and in the co-authored publication Griffiths et al. (2013b).

- Nano gold cores with palladium outer shells deposited via a wet deposition technique onto carbon black supports. Each Au core is 20 nm in diameter, but two different Pd core shell (CS) thickness of either 1 or 10 nm; CS1 or CS10 respectively. Covered in Chapter 7, and founded on the collaborator publications of Celorrio et al. (2012a) and Plana et al. (2013).

These materials were assessed in the first instance since they were those showing promising CO_2 conversion performances within a wider consortium of researches developing CCU processes (see APPENDIX A:). Additionally they can be considered well targeted materials since MWCNT growth via CVD is widely touted as being the promising lead when moving towards industrial synthesis scales (Kushnir and Sandén 2008; Zhang *et al.* 2013). Furthermore covering two contrasting wet deposition

techniques affords insight into where commonalities and differences arise in their life cycle impacts.

The related life cycle work reported in this thesis was conducted in close contact to those involved in the direct synthesis of ENMs. This facilitated the collection of detailed inventory data, which is severely missing from LCI datasets, for other LCAs to begin assessing potential benefits of ENMs. Transparent and accurate accounts were constructed of the discernable materials, chemicals, energy use, and other associated flows as well as the equipment used across the life cycle of the tested ENMs.

8.1.1 *ENERGY INTENSITY*

A key similarity across the formation routes of the different ENMs assessed is the high energy requirement involved in their synthesis. For all tested materials the impacts of the electricity consumption was a very dominant aspect, especially with regard to GHG impact and at least half of the other categories assessed (see impact categories in section 3.3, page 42).

The major impacts of the Fe-Pd-Silica catalysts, were due to the calcination stages where heat treatment was needed to convert the iron/palladium precursors into the active catalyst ENMs.

In the CS electrode coating gate synthesis, heating was followed by sonication to bind colloidal ENMs to the carbon substrate were found to be the most energetic aspects of the life cycle.

8.1.2 *METAL DOMINANCE*

In chapter 5 and chapter 7, precious metal nanoparticles are the active materials present in the resultant formed heterogeneous and electrochemical catalysts. Albeit for different end-applications, their synthesis was broadly similar, with the deposition of colloidal particles of metal onto inert porous substrates.

Catalysts with precious metal content would see the impacts of their use more dominant than synthesis energy for many of the impact categories assessed, these include, but not limited to: toxicity, photochemical oxidant and particulate matter formation, terrestrial

acidification, eutrophication, water depletion and metal depletion. This trend was especially apparent when increasing quantities of palladium were added to the FePd-SiO_2 catalysts (chapter 5). The gold and palladium used in the electrode coatings (chapter 7), were found to have very similar influencing effects from their metal content, although nominally similar impacts for both CS materials formed the thinner shelled palladium resulted in proportionally higher loadings of gold in final application; a more impactful metal overall.

The burdens of precious metal usage lie early in their upstream life cycles, where the mining and refining of ores into pure materials streams are intensive and environmentally polluting activities.

8.1.2.1 Recycled content

The high impact use of precious metals in the context of the formed ENMs meant that the results were more sensitive than most life cycle inputs to the representative LCI model and assumptions taken. Gold and palladium exist as mixtures of primary and recycled/secondary content. This mix is subject to temporal and spatial variations, the most recent data for the global average recycled content (RC) of these materials were taken. The Ecoinvent Database v2.2 (2010) mix for palladium was found to have a low RC, as discussed in chapter 5, consequently inflating the likely impact of the used metal; a scenario analysis of different sourced palladium provided a more representative account.

8.1.2.2 GHG Impact

Interestingly, if carbon foot printing (CFP) – GHG impacts - were to be considered in isolation for the ENMs assessed in this thesis, results show electricity to be in excess of 60 to 95% of total life cycle gate impacts. Although the precious metals, where applicable, show an effect on the CFP results, arguably this is not significant or adequate enough to convey the true environmental burdens, and consumption of finite resources through their use.

8.1.3 *INFRASTRUCTURE IMPRINT*

The studies in this thesis considered the impacts of capital equipment used, and the embodied impact in which synthesised ENMs would inherit from these devices. Including the effects of infrastructure addresses an identified gap in the LCA of ENMs (Upadhyayula *et al.* 2012). The need to explore the impacts of capital equipment impacts in the formation of ENMs has been a matter to address from an early stage in the efforts of quantifying the impacts of these materials (Klöpffer 2007).

Due to the nature of the assessed laboratory equipment, there is likely to be uncertainties in accounting for the impacts at this scale. However, their inclusion is an indicative account of the background impacts that come with ENM synthesis, a class of material already proving to have more intensive synthesis routes than traditional materials (Kim and Fthenakis 2012). With reference to specific ENM case studies:

- For the MWCNT assessed equipment impacts -after energy use- was found to be the second largest impact, above feedstock chemical use and acid purification treatments (Griffiths *et al.* 2013a).

- In the synthesis of FePd-SiO_2, and CS catalysts, the infrastructure could be considered a trace impact in the context of other life cycle contributors. However, infrastructure is comparable in many of the impact categories to the summation of the non-direct chemicals (i.e. involved in synthesis but not present in final product) used in the synthesis routes.

- A potentially anomalous, yet equipment derived impact, results in infrastructure use in the synthesis of FePd-SiO_2 catalysts bucking the wider trends to dominate the ozone depleting potential; this is down to the use of chemically resistant fluorine parts present in the synthesis equipment (discussed more deeply in chapter 5).

8.1.4 *OTHER CHEMICAL CONSTITUENTS*

In the production of the different ENMs, relatively large (in comparison to quantities of final product) quantities of precursors, reactants and solvents are required. The resultant impacts of these, however, are almost negligible across all assessed impact categories.

In the heterogeneous CO_2 conversion process, iron content catalysts were chosen due to the relative abundance of iron ore, and their potential for good catalytic activity. Indeed in terms of the LCA of the iron precursors the iron content was on the lowest ends of the impacts involved in the synthesis of the materials; not unexpected since iron is a relatively low impact material in comparison to other more precious metals and finer chemical products. The near negligible iron-specific impacts are empathised when considering the iron nitrate precursor was mostly dominated by 90% due to the nitric acid content. The palladium and gold precursor solutions conversely are dominated by the respective metal contents

8.1.5 *END-OF-LIFE FINDINGS*

Another impact often missing from LCAs of CNTs are the end-of-life (EOL) disposal impacts, largely due to uncertainties surrounding their activities (Breggin and Pendergrass 2007; Franco *et al.* 2007) and only recent relevant standards in place specifically aimed at addressing ENM waste streams (BSI 2012).

An incineration stage, capable of complete combustion of MWCNTs was modelled; its influence was found to be the second largest impact after process heat requirement during MWCNT growth. It is advised that this activity is included, as an associated part of CNT use 'baggage', and a necessary step in the mitigation of potential CNT threats, many of which although potentially severe (Lam *et al.* 2006; Peralta-Videa *et al.* 2011) have not been wholly quantified.

Since $FePdSiO_2$ and CS ENMs have much of their embodied impact due to their precious metal content, no disposal stages such as incineration was considered as this would result in these material streams being irretrievable. Instead hypothetical E-O-L material recovery stages were modelled, thus from a life cycle perspective recouping the initial burdens associated with their usage. Material developers were consulted to gain

an understanding of the likely routes in which materials could be retrieved using the available laboratory equipment, this founded the basis of a model.

An acid treatment, using a mixture of hydrochloric and nitric acid, and a sonication stage would allow the dissolution of metals from the ENMs in to a recoverable solute form. LCIA results indicated that although benefits were seen in the categories where metal content dominated, the additional high energetic sonication step added more burden to approximately half of the impact categories. However, this result is sensitive to the source of electricity used, when a renewable wind source is used in place of the UK grid there are across the board benefits seen for the metal recovery stage.

Material recovery benefits were only present for materials with precious metal content, for the iron only $FeSiO_2$ and formed CNT catalysts efforts to recoup iron post catalytic use, would be more impactful than not retrieving the iron. Although this model is considered an early scoping account of likely burdens it is indicative that some materials can return tangible value to the technosphere at the end of their useful lives whereby others cannot; and EOL strategies need to be mindful of this from early stages of new material production.

8.1.5.1 End of life modelling limitations

The recovery of the ENM metal content is founded on a first approximation model. To account for inefficiencies in the process only 70% of deposited material is seemed retrievable. Furthermore the allocation of impacts is governed by the nature of how the ENMs are integrated into their end application. FePd-SiO2 catalysts are powdered masses which can be placed in a sonicator with a maximum capacity in terms of stoichiometric retrieval.

CS coatings are affixed onto the electrodes, thus the capacity of the sonicator is filled more with bulk non-ENM material in addition to the immediate carbon black substrate in which they are bound to. Being connected to a larger bulk item offers less retrieval per operation; arguably this allocation is a crude model, but is in alignment with current and implementable laboratory setups.

8.2 LIFE CYCLE INVENTORY DATA

Chapter 3 details the approach used to gather LCI data in this thesis. The LCI was striving for a comprehensive account of the key and distinguishable material flows involved in the final deployable ENM.

8.2.1.1 Energy measurements

The impacts of energy use are a combination of direct energy used in different activities and those fugitive in the life cycles of the materials and other flows entering the system. Energy provision during all assessed synthesis and operational processes was in the form of electricity. Direct measurements of the electricity consumption were conducted using a power meter.

8.2.1.2 Infrastructure

The static components of the synthesis and operating parts of the life cycle were established. In the first instance this required identifying all discernable aspects and activities present and performed in the laboratory, directly involved in the synthesis and operational activities. Non-direct equipment such as sampling and analysis equipment were placed outside of the assessment scope.

The generation of infrastructure data followed a broadly similar approach of:

1. partial disassembly,
2. direct measurements and materials categorising of componentry parts,
3. discussion with equipment users,
4. consulting equipment manuals, contact with equipment manufacturers (rare)

The outcomes of this approach resulted in the best capture of equipment available at the time of conducting the LCAs. Reaffirmation of the accuracy of material coverage occurred during the –albeit rare- communications with material equipment manufacturers. In addition to establishing the absolute environmental impacts arising from the material constituent parts, the operational lifetimes and maximum capacities of

the different devices was also obtained. This allowed for more representative allocation of infrastructure impacts to the formed materials to be achieved.

Many of the LCA models analyse the effect of changing laboratory practices to be more akin to a streamlined production line. In allocation terms this meant a move from daily one-off batch synthesis activities over the equipment lifetime, to continual operation with respect to the time period of specific activities related to the total operational lifetime of the equipment. This lean account always has the immediate effect of reducing the imprint of the infrastructure equipment itself. In addition, for the growth of the MWCNTs, less time within the reaction infrastructure offered further benefits of reduced energy and Argon carrier gas consumption.

Furthermore, the disaggregate form and detail of the infrastructure LCI data allowed further adaptation to estimate changes with respect to: improved material throughput, effects of increasing scales of production, and an appreciation of the recoverable material constituents; for net reductions in the through life use of the devices.

The accounting and reporting of the equipment LCI data will allow others to confirm, adapt or substitute should the systems change or alternative production methods be used.

8.2.1.3 Chemicals and materials

The ENMs assessed were all formed via chemical synthesis routes. The LCA work took an account of all chemicals and materials involved in the synthesis of the formed ENMs. In many cases the more common substances such as: de-ionised water, methanol, pure metal salts used could be modelled using representative LCI data from the Ecoinvent database. However, due to the plethora of compounds utilised, there was often a need to produce bespoke datasets for the flows entering the assessed system. Missing data for chemicals is an existing challenge for the LCA community (Hischier *et al.* 2005a).

Despite contacting many suppliers during the course of this research no forthcoming data was supplied of any accurate or meaningful form to generate LCI data. The degree of effort in producing these was dependent on the extent in which coverage of precursor constituents were included within the available LCI databases. Thus the approach taken,

as outlined in chapter 3, was an amalgamation of; chemical mass balances via stoichiometric relationships of precursors, and the use of proxy and representative data. However, in certain instances there was a need to produce inventory data from 'the ground up', in these cases no data was found to representative of the synthesis route. The produced inventory datasets include:

Ferrocene: present as the catalysing agent for MWCNT growth, studies to date had not captured the impacts for the catalyst initiator used in growth (Upadhyayula *et al.* 2012). The amalgamation of patent and literature data, together with collaborative efforts with chemical process modellers produced a detail life cycle account of the gate impacts of ferrocene synthesis.

Naturally derived acids: in the formation of the CS electrode coatings both citric and ascorbic acids are used. The synthesis of both could be appreciated as analogous, at least in major fermentation processing aspects, to that of the use of bio-feedstocks used in ethanol production. Choice likely feedstocks and respective product yields were considered.

Silica: Silica is a widely used substrate support for heterogeneous catalysis, due to its stability at various temperatures, its ease of synthesis and control over the physiochemical properties; particle dimensions and pore size. Consulting related literature and communication with a producer formed much of the modelled process.

In the context of the LCA studies within this thesis, the impacts of the generated inventory data were found to be very low in comparison to other life cycle stages; due to the simple nature of the synthesis steps, and relatively benign nature of the constituent materials. However, these finding direct focus onto the more impactful and influential life cycle elements, furthermore in other systems the quantities and use profile of these materials might be more key, and thus the data would be of value in those systems.

8.2.1.4 Waste Flows

With regard to chapter 4, characterising the exhaust species formed during the CVD growth of MWCNTs allowed an appreciation of likely impacts if these emissions were released to the atmosphere.

When modelling chemical synthesis routes for other ENMs throughout this thesis, the generated volume of waste streams would be considered as industrial waste to water treatment plants. Generalisation in this way is largely unavoidable when so much uncertainty surrounds the likely end of life treatment, and indeed without consideration of other processes that at industrial scale might make use of waste/by-products. The impacts of waste treatment were always found to be negligible in comparison to other gate synthesis and in-use impacts of the materials and processes.

8.2.2 *LIMITATIONS OF INVENTORY DATA GENERATION*

In addition to the already stated assumption there remain a series of limitations with regard to the coverage and representativeness of the conducted LCA studies.

Although major chemicals, materials and energetic conisderations are taken into account of generated inventory datasets, for the most the part the capture of reaction vessels and plant infrastructure involved in upstream chemical synthesis routes has not occurred with great detail. Uncertainty over the practices and restricted data availability meant that assumptions in line with similar covered within the Ecoinvent database occurred. Similarly for infrastructure inventory capture, materials elements are covered but assembly and through-life servicing ignored. However, when assessing Ecoinvent datasets, and other LCA studies, which cover the influence of these elements are typically substantially lower impact contributors, when compared to the material and energetic system flows.

Reliance often on proxy datasets used for material/chemical constituents, either through drawing comparisons between similar processing routes or formed end material. Where available, additional tools would be used such as Finechem (Wernet *et al.* 2009) for molecularly similar petrochemical products, to provide additional information and verification of chosen data.

Although all reasonable efforts were taken to gather representative datasets, there were limitations in doing so:

- Significant time is invested in gathering and verifying data choices, ultimately meant that cut-offs and boundaries had to be drawn.

- Equipment manuals and manufacturers, lacking in accurate and useful data for the LCI generations.

- Impacts are specific to the laboratory equipment to hand, appreciably these could differ between laboratories, to address this with only including directly used devices.

- Uncertainties arise with what form infrastructure might take in larger scales of deployment, in an attempt to address this lean setups considered laboratory device inefficiencies and redundancies.

- Ecoinvent is representative but not necessarily a wholly accurate or faithful account of actual materials used.

8.3 IMPROVED SYNTHESIS PRACTICES – LEAN MODEL

The impacts of forming the different ENMs at the laboratory scale provide benchmarks for those using them, allowing the contributing factors behind the material environmental footprints to be appreciated. Laboratory practices are not likely to be representative of how these emerging materials would be synthesised at more established and optimised process routes. Therefore, an approach to present the likely impacts that would remain for more efficient synthesis routes was conducted.

Appreciably, ENMs were formed via different production routes, and thus no universal scaling factor can be applied. The details behind the specific approaches used are presented in each of the respective chapters; however Chapter 3, section 3.7 provides the general thinking behind the approach, which can be outlined as:

- Maximising infrastructure capacities

- Recycle unused feedstocks

- Reduce / retrieve high impact embedded materials

Explore the effect of switching electricity source from UK grid to a renewable wind generation source; a crude way to decouple and consider the impact of using electricity from temporal and spatial factors. Figure 8-1 provides a snapshot account of the

resultant environmental impacts that follow the adoption of these changes. It can be seen for all materials that significant cradle-to-gate impact reductions are achievable. Progressive improvements are witnessed as the model considers more of these likely process changes. Although the degree of improvement is dependent on the materials assessed, there are clear unifying findings present for these different ENM classes.

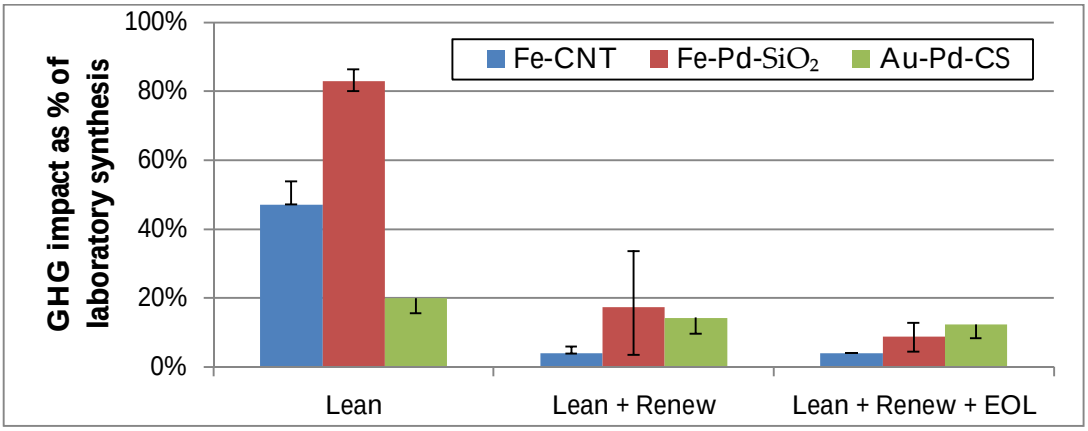


Figure 8-1 Comparison of relative changes in GHG impacts of ENM formation impacts, for different scenarios. Error bars show ranges across the different ENMs.

With reference to Figure 8-1: bars for F-CNT, show upper bound impact of Fe_Dec_CNT (see chapter 4); Fe-Pd-SiO2 shows the range across the eight different catalysts (chapter 5); Au-Pd CS shows the lower impact but worse net performing catalyst (chapter 7).

8.3.1 *LEAN*

Common to all materials are the inefficiencies of the laboratory scale, the GHG impacts of this scale are the reference 100% of Figure 8-1. The guiding principle of a lean model, are that activities and practices seek to minimise the redundancy in the capital infrastructure equipment used, and enhance the flow of materials through the synthesis equipment.

MWCNTs witness a large single-step improvement when moving towards the lean setup. MWCNT growth is dependent on the reactor reaching a set-point temperature, at laboratory scale this means a heating and cooling period is in place between batches, the latter for safe non-oxidising retrieval of the MWCNT product. More continuous processes are under development, which would put an end to batch-like cyclic

heating/cooling activities (Li *et al.* 2004; Agboola *et al.* 2007), the lean setup could be considered as indicative of what the associated impacts might look like.

For MWCNTs, the intensity of energy and its resultant impact was, arguably, an established finding in the field (Upadhyayula *et al.* 2012). However, whilst conducting the research it was found that the majority of this energy is spent on periods where the formation of the MWCNTs was not directly occurring. But rather in heating and cooling activities; detailed more in chapter 4, and Griffiths *et al.* (2013a). By interrogation of this it was found that significant reductions in energy usage would occur if the process were to move from batch synthesis laboratory practices to a more continuous production route.

With focus on the specific energy requirement of MWCNT materials, previous reviews of ENM synthesis (Gavankar *et al.* 2012; Upadhyayula *et al.* 2012) focused solely on carbon nanotube products. Conclusive findings are the recognition that CNTs are highly energy intensive materials in the region of 1 – 900 GJ/kg, orders of magnitude more so than conventional 'high energy materials' such as primary aluminium production ~200MJ/Kg. The laboratory case LCA of the MWCNTs via a chemical vapour deposition route, detailed in Chapter 4, had comparable impacts to those reported by others. However, this further analysis via the precautionary 'lean modelling' approach indicates that many wider environmental impacts could be reduced by an impact-wide average of approximately 50% (90% reduction when renewable electricity and feedstock is modelled).

Fe-Pd-SiO_2 demonstrates the least potential for improvement with the adopted lean model. Much of this is due to the majority of incumbent impacts involved in the synthesis; appreciably removal of these is not possible as it would have immediate repercussions on the ENM in-situ catalytic performance. Similarly, the different activities of synthesis were not adjusted as these would have likely effects on the material deposition with relation to substrates.

Au-Pd core shell particles demonstrate a large drop when moving towards a lean model. The underutilisation of the oven at the laboratory scale is wholly responsible for this reduction. Appreciably the impacts of the Fe-Pd-SiO_2 could be foreseeably

minimised, however, and in alignment with the conservative representative approach, the laboratory device capacities were not capable of such process flow improvements.

Further work is required for these processes, which require advancement in parallel with the move towards more industrially relevant scales of production. However, the lean results presented throughout this thesis are 'take-home values' for a conservative and achievable ENM process within the confines of current technology systems.

8.3.2 *RENEWABLE ENERGY USE*

As discussed previously, all ENMs are energy intensive, the impacts of energy source is thus a sensitive life cycle consideration. When modelling the use of a renewable energy source, the likely GHG and the majority of other impact categories significantly reduce, as discussed in chapter 3. The implication of adopting an all-renewable mix – in this case a generic European average wind generation datasets- is a topic of wider debate, however, it is worth noting the possibility to de-couple ENM synthesis from fossil fuel usage, something the production of major materials such as steel and concrete are inherently reliant upon.

The inclusion of a renewable scenario is of benefit when appreciating that wide variances exist between country electricity mixes; appreciably for countries with less intensive grids than the UK, such as those of Nordic and other European nations, will sit somewhere between the lean and lean + renewable results. For the Fe-CNT case, a small portion of renewable gains are also in part due to the use of renewable hydrogen; as discussed in chapter 4, but with an appreciation of hydrogen impacts (see chapter 2) this is a much lesser contributor.

8.3.3 *END OF LIFE RECOVERY BENEFITS*

As discussed throughout relevant EOL sections throughout the thesis, the implications of EOL treatment are not best presented when considering the sole GHG impact indicator. Modelled benefits are for other categories such as minimising toxicity and resource imprint/consumptions effects. Indeed disbenefits are seen, as previously discussed, for materials which do not have precious metal contents.

The additional offsets without retrieved benefit can be appreciated in Figure 8-1, whereby the lower-range impact of Fe-SiO_2 (without Pd) catalysts have increased for the EOL case, similarly the CNTs show higher life cycle impacts when attempting an EOL activity.

8.4 NANO-SPECIFIC FINDINGS

In addition to LCA 'good practice' of clear reporting of inventory data sources and assumptions, the nature, size, morphology and amount of ENM being produced, and potential exposure points along the life cycle are also reported. This is in accordance with current recommendations by current thinkers in the field; especially those seeking to adopt risk assessment practices and integrate these with the LCA process to better inform those of the potential environmental impacts and risks associated with nanotechnologies (Franco *et al.* 2007; Som *et al.* 2010; Hischier 2014).

As discussed in chapter 2 of this thesis, a present lack of life cycle impact assessment methodologies (LCIAM) exist for ENMs in the environment. Therefore, a question mark remains with regard to these potential life cycle impacts within the LCA case studies presented in this thesis. However, much of the ENM risk is expected to be mitigated for the applications covered, since their use is in a non-dispersive means, and within closed system. It is expected that the EOL take back of these systems will be part of the roll-out of such technologies, and that potential hazards are managed by suitable working practices; to at least make materials benign or prevented from environmental release; further LCA work will be needed to cover the system impacts of such processes.

A methodology based on USETOX (Rosenbaum *et al.* 2008) impact assessment criteria was developed by Eckelman *et al.* (2012) for CNTs release into the aquatic environment. Although the modelled impacts are a first estimate in this field, they were found to be the only LCIAM tool available at present time. By using the model, the results show that the unhindered release of the formed CNTs would potentially in the worst case, have more damaging aquatic ecosystem impacts than any of the other activities associated with the gate synthesis of the CNTs.

8.5 FINDINGS FOR THE OPERATIONAL PERFORMANCE OF THE CO_2 UTILISATION TECHNOLOGIES

The study of ENM gate impacts in isolation is an informative aspect in identifying where incumbent impacts lie, and the potential for mitigating factors at the root cause of formation gate impacts. However, the only way of determining the net benefit of these materials is to assess them in the context of a real application. This becomes more insightful when the materials are compared on a functionally equivalent basis to competing technologies.

This research sits in a niche field, which has gained momentum in recent years (Griffiths *et al.* 2013b; von der Assen *et al.* 2014), exploring the potential for materials and technology solutions of carbon capture and utilisation (CCU). Two CCU technologies were assessed in this thesis:

- a heterogeneous catalysis route, which combines the reverse water-gas shift reaction with the Fischer-Tropsch process. Converting CO_2 and H_2 feedstocks into hydrocarbons. Chapter 6.
- an electrochemical process, reducing CO_2 within an aqueous cell setup into carbonaceous compounds. Chapter 7.

Assessing the performance of these technologies required oversight of the required energetic, material and feedstock flows of the operating processes. These are duly covered in the relevant chapters (chapter 4 through 7). The LCA work concentrated on the relative impacts in which the ENMs imprint in relation to these other flows contributed to the overall feasibility of these as CO_2 abatement solutions, and other related environmental impacts that arise through their exploitation.

8.5.1 *SELECTION OF BEST OPTIONS*

The impacts of forming materials appreciably differ on the intensity of their synthesis route, and the embodied impacts of their constituents.

In chapter 5, the formation of iron-palladium-silica (Fe-Pd-SiO_2) ENMs are covered, from considering their end application as CO_2 converting catalysts. A key finding is, that

although the impacts of Pd-containing catalysts were the largest from the perspective of their cradle-to-gate synthesis. Their improved functionality over iron-only, and indeed the other lower impact MWCNT catalysts (Chapter 4), meant that from the perspective of a meaningful in-use period, they would offset this initial burden before lower impact (iron-only) catalysts could. Fe40Pd1 was found to be the best RWGS-FTcatalyst, producing more quantity and better mix of HCs, with an overall greater GHG offset, and with the lowest specific environmental impact in comparison to the other palladium-containing catalysts.

Electrochemical process findings again show that, in this case, a comparatively more impactful catalyst - owing to more gold loading - was able to offset its impact at a quicker rate over a set operating period. Thus CS1 was a better catalyst than CS10. Such findings highlight the importance of considering the end application and performance of ENMs, to evaluate and justify their high embodied impacts.

In addition to material choices the iron activated MWCNTs, which significantly outperformed the iron decorated variant, were assessed over a wider range of reaction conditions. A series of attributing factors including the temperature, pressure and flows of feedstocks were balanced and assessed in relation to the respective catalytic performance. Due to the infancy of the technology, much of the analysis was founded on theoretical calculations in the absence of full process data. This approach provided meaningful outcomes in terms of perceived benefits not always coming at best life cycle costs. Although notably for the best RWGS-FT reaction condition this aligned with best net life cycle impact; a 2.5 bar reaction pressure, 370 °C, and 8 sccm feed flow.

8.5.2 *HYPOTHESISED CCU PROCESSES IMPROVEMENTS*

The ENMs assessed were developed to make use of CO_2, thus the net GHG potential of the processes were the initial starting points for the assessment.

Processes at the laboratory scale have not been close to meeting carbon neutral process operating envelopes. However, a key and over-arching finding when discussing the specific case studies within this thesis, is that the RWGS-FT and electrochemical routes both have the *potential* to offer both net negative GHG (and other impacts) across their life cycle. Additionally, the products formed are useful compounds of high societal

value, substitutable with many commodity chemicals and fuel sources. The presences of products were directly measured for the RWGS-FT processes, however remain as predictions of likely products for the electrochemical process until further research of the collaborator groups.

The analysis work within this thesis is founded on robust and transparent inventory data, collected directly from the developed materials and processes. Having confidence and insight into the inner-working of the processes allowed for the forecasting of likely environmental impacts that would arise should the processes develop from their early prototype stages into larger processes scales.

- **Functionally equivalent** systems were compared, on the basis of cradle-to-gate life cycle on a mass basis of products formed, with consideration of any other identifiable potential co-products.

- **Technology scales** were explored to facilitate fairer comparison between laboratory scale technologies with more established industries. A precautionary approach of identifying areas and activities within the life cycle that would be affected, or omitted by altering, improving, scaling of technologies. Considered as an early scoping or forecast, unlocking the technologies commercial potential from an environmental perspective.

- **Upper-bound limits of performance, or the 'ideal',** were presented as a process-specific metric. Based of stoichiometric relationships, for the conversion selectivities measured by the process. Assuming a 100% conversion of feedstock to product. The maximum quantity and subsequent offset of formed products could be measured.

8.6 DISCUSSION OF CCU PERFORMANCE

Considering the performance at laboratory bench scale, and exploring likely process changes with scales and different case scenarios the overall GHG performance of both RWGS-FT and Electrochemical CO_2 conversion route are detailed in Table 8-1 and Table 8-2, respectively.

8.6.1 *HETEROGENEOUS RWGS-FT GHG PERFORMANCE*

It is clear that the RWGS-FT route is highly sensitive to the energy requirements of the process. In short, at laboratory scale the process is requiring heat input, delivered via electrical elements and represents >99% of the GHG impact.

Table 8-1 GWP impact of a laboratory and representative industrial RWGS-FT process. Results for Fe40Pd1 catalyst, 5000 hour lifetime, 30 year infrastructure.

Left column colour key:	Heat requirement		Autothermal (Heat in = heat out)			Heat out for co-generation	
	Catalyst	**Infrastructure**	**H_2**	**Energy**	**CO_2**	**HC Offset**	**NET GWP [$kgCO_2eq./h$]**
Laboratory	0.2%	0.6%	0.1%	99.4%	-0.3%	0.0%	**6.2E-02**
Lab + Renewable (*Ren*)	7%	27%	3%	76%	-12%	-1%	**1.4E-03**
Lab	29%	111%	14%	-	-49%	-5%	**3.5E-04**
Lean + EOL+ Recycling (*Rec*)	39%	90%	8%	-	-28%	-8%	**2.1E-04**
Lean + EOL *Rec* + *Ren*	9%	134%	12%	-	-42%	-13%	**1.4E-04**
Lean + EOL Co-gen +*Rec* + *Ren*	10%	163%	14%	-21%	-51%	-15%	**1.1E-04**
Lean (10%) + EOL Co-gen + *Rec* + *Ren*	22%	35%	31%	-46%	-110%	-33%	**-5.3E-05**

The switch to lower impact renewable electricity source, drops the operational impacts significantly. However, meaningful improvements are only witnessed once an 'industrially relevant' process scale is considered. This is discussed in chapter 6, in brief it has been modelled that larger scales would exploit the exothermic nature of the RWGS-FT reaction. At smaller scales the increase in heat is immeasurable due to the small quantities flowing through the reactor. However, at larger scale Fischer-Tropsch plants require continual cooling to prevent overheating, and indeed can use the cooling stream as a source of power generation (Liu *et al.* 2010).

Autothermal, heat in equal to heat out, conditions show operational impacts two orders of magnitude improved over the laboratory, incremental improvements including lean

and end-of-life material recovery with renewable sources show further improvements to this.

Electricity co-generation needs to be realised in order for the process to begin to approach potentially net GHG negative impacts. Moreover, with appreciation of the contributing aspects within Table 8-1, the process would be net negative even without the consideration of the environmentally beneficial offsets attributable from not sourcing the produced hydrocarbons from traditional routes, 'HC Offset'. Thus meaning the process would be an actual carbon sink within its own right. The target for technology developers is to produce the incumbent equipment infrastructure to ~10% of the specific amount of the lean laboratory case in order to meet carbon negative operation. More specific infrastructure reduction targets are discussed in chapter 6.

8.6.2 *ELECTROCHEMICAL CONVERSION*

The operational profile of the electrochemical route differs from the RWGS-FT process. Initially it is the infrastructure impacts that are prohibitively large. However, as hypothesised in chapter 7, the impacts of the laboratory operational cell are many orders of magnitude over-specified for the amount of electrical current being delivered at the electrode. Thus, the lean model reflects not only the enhanced CS1 catalyst improvement, shown in Figure 8-1, but more importantly the significant reduction in infrastructure burden; operation is now approximately a hundred times less impactful (from $x10^{-6}$ to $x10^{-8}$).

Table 8-2 GWP impact of assessed electrochemical process. Results for electrode material CS1, 5000 hour lifetime, 30 year infrastructure.

	Catalyst	Infrastructure	Pt Counter	Electricity	CO_2	Offset HC*	NET GWP [$kgCO_2eq./h$]
Lab	12.6%	87.6%	1.8%	2.8%	-1.8%	-3.0%	**4.1E-06**
Lean	326%	1.8%	36.4%	356%	-232%	-388%	**3.2E-08**
Lean + Renewable	84.5%	0.1%	49.8%	46.5%	-30.3%	-50.7%	**2.4E-07**
Lean + Renew + EOL	52.5%	0.2%	6.7%	2.5%	-60.5%	-101%	**-1.2E-07**

** Likely offset since exact presence of any HCs formed is unknown.*

From Table 8-2, the renewable electricity source expectedly improves the process, but the EOL recovery of precious gold, palladium, and platinum is necessary to achieve net beneficial impacts. Thus illustrative of the benefits only being perceived if a holistic operational system is rolled out. Unlike the RWGS-FT process, no further co-product has been identified, and with CO_2 conversions as high as they are likely to be, the process cannot in its own right be considered GHG negative, instead relying on HC offset to achieve favourable net operating conditions.

8.6.3 *ENM EFFECTS ON CCU PERFORMANCE*

Researchers were interested in realising the effects that improved catalysis performance would have. Therefore idealised best case conversion levels were used. The high faradaic efficiency (>90%) for the CS1 electrode, represented an upper-bound performance unlikely to be bettered; and thus was taken as the ideal. The selectivity of the products, and indeed nature of electrochemical products was hypothesised to be very likely based on other similar cells (Spinner *et al.* 2012; Taheri Najafabadi 2013), and split equally between three likely products; carbon monoxide, formic acid, and methanol. For the RWGS-FT process a 100% conversion has been modelled, setting a ceiling for researchers, and the ideal selectivity towards formed products is based on the Anderson-Schulz Flory distribution of an optimally running Fischer-Tropsch process.

The in-use performance of the ENMs are exhibiting very promising CO_2 conversion performances even at this early stage of material research and wider process integration and development; and are not the limiting factors in operational process feasibility; as many predicted and arguably vindicating the interest in the ENM field. However, this does not imply that the materials are in the form of finished solutions, indeed findings indicate once final optimisation of materials and process conditions are achieved, indeed even better catalyst performances were witnessed as alluded to at the end of chapter 6, and covered in more detail in the collaborators PhD thesis (Rhodri Owen, PhD Thesis, University of Bath, 2014). Once these are more finalised, and if progressed to wider scales of manufacture, many of the inherent synthesis impacts due to inefficiencies in material process flow and energy usage will be overcome. However, crucial factors in these technology environmental credentials are the extension of operational life and better EOL recovery stages, to recoup initial high impact materials.

8.6.4 *IMPLICATIONS ON FORMED PRODUCT IMPACTS*

For both the RWGS-FT and electrochemical route.The formed products can again be *potentially* formed to be environmentally competitive in comparison to equivalent counterparts formed via the traditional and most established fossil fuel and petrochemical origins.

The electrochemical route investigated has the potential to produce products at a lower environmental burden than current routes of production. For the RWGS-FT process, however, with continual improvement towards net-negative impacts, there is the potential for net-negative GHG impact products, the nature of which mean the more CO_2 is 'locked away' inside the product than has been incurred in getting it to this point. Net-negative products represent carbon sinks being created, with the carbon content of the formed products and co-products outweighing the GHG emissions incurred in their formation. This means that genuine CCU objectives are being achieved; a lowering of anthropometric climate change impacts across the whole life cycle of the formed products.

8.6.5 *DISCUSSION OF RELATIVE OFFSET IMPACTS BEING ACHIEVED*

With the benefit of comparing both RWGS-FT and electrochemical routes assessed directly in this chapter, an appreciation of the relative hydrocarbon offset impacts being achieved is possible. These offsets are founded upon reference datasets which are representative of the most likely routes of hydrocarbon production, these were found sourced from (Ecoinvent Database v2.2 2010), and discussed where used in chapter 6 and 7.

The products being formed by the electrochemical process are equivalent to a greater relative offset per amount of CO_2 converted than the RWGS-FT process; this is down to two compounding reasons. Firstly, the materials being offset by the electrochemical process are of a higher relative GHG (and majority other) impact. Secondly, the electrochemical process consumes less CO_2 in making these products, since they have a lower relative carbon atom content. This secondary measure can be considered to better take into account the returned benefit on the initial quantity of CO_2 being consumed by the respective processes. Simply put, if a product with five carbon atoms, does not

result in an offset five times larger than a product only consuming one CO_2 molecule; then this represents a loss of potential total offsets for the quantity of CO_2 being converted.

This approach is an arguably crude metric, but considering the additional feedstock for the electrochemical route is water, and the hydrogen input necessary for the RWGS-FT process is an order of magnitude less impactful than the CO_2 feedstock used. The approach can be considered a representative capture of underlying reasons for the better performing electrochemical offsets. This finding is illustrated in Figure 8-2, whereby even on a mass basis electrochemical process product mix is 1.6 times more beneficial (offsetting), and when normalised to consider carbon content this increases further to almost five times as impactful.

Considering that GHG impact is a valid metric in terms of CCU process comparisons, however, this does not take into account the market demand for the products being formed, and indeed represents a snapshot; hydrocarbon extraction and refining process could well increase in future years, thus increasing the potential offset of the operating process.

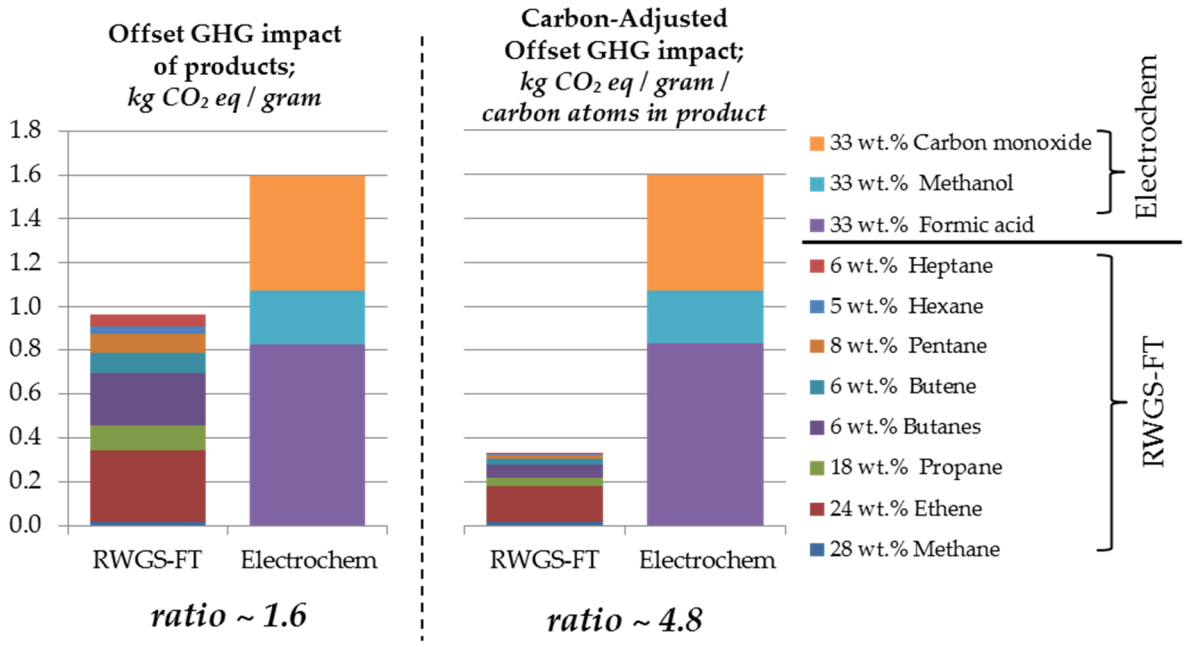


Figure 8-2 GHG impact of 1 gram of product formed via either RWGS-FT process (modelled on ideal product mix) or electrochemical process (top). This impact normalised to carbon content of the formed product, i.e. relative quantity of CO_2 locked in (bottom).

8.6.6 *CCU BOUNDARY*

The scope and boundary of the LCAs cover activities involved in CO_2 capture, through conversion, to production of final products.

The LCA system boundaries have not been expanded to cover the final use of formed products, as there are great multitudes of uses and downstream life cycles. Indeed, as fuels they might very likely be immediately combusted, instantly releasing CO_2 into the atmosphere. Never the less, the study outcomes are important as:

- GHG is not the only impact to consider, the production of products void of localised effects of petrochemical drilling and mining will mean significantly less toxic, and localised environmental damage.
- secondly, the products formed could well be used to form materials such as plastics. This would lock CO_2 away for a longer time period.
- and finally, the use of a GHG-negative to gate fuel, will carry with it a deficit in comparison to the equivalent formed through routes which have proven GHG-positive impacts; thus part-mitigating the use of the products in existing applications.

Wider scope of assessment would be needed to validate entire life cycle GHG, and other impact, offsets achievable through CCU. Limitations to the full boundary can be appreciated as being non-complete coverage of distinct product stream separation. However in the case of the hydrocarbons formed at the exit of the RWGS-FT reactor the products are at the temperature that commercial petrochemical distillations towers heat products before separation. Furthermore, heat provision in the refinery process is the most dominant aspect of the gate impacts of the respective products formed (Althaus H.-J. 2007). More uncertainty exists for the electrochemical cell process, since products will need in-situ recovery from the electrolyte solution during use; this remains uncertain due to the actual method of likely separation, dependent on the first instance on defining the exact products being formed at the electrodes.

8.7 GUIDANCE AND COMMUNICATION TO TECHNOLOGY DEVELOPERS

The direct and immediate contact which afforded the insight required when constructing inventory data, also facilitated direct dialogue between the material and technology developers, so that an appreciation of implementable process change could be explored. Major outputs of the collaborative work allowed the determination of relative impacts within the life cycle, specifically addressing;

- those attributable to the working practices of the laboratory synthesis; appreciably not designed to cater for efficient throughput of materials.
- other impacts that remain but can be minimised or mitigated through the choice of process inputs.
- the inherent impacts, those present due to the very nature of the materials and processes being developed. Such as amount of energy, and quantity of precious metals needed.
- changes likely with scale: estimating enhanced efficiency of throughput, lower specific infrastructure, and the exploitation of realisable co-products.
- effect of material recycling loops on the life cycle.

Using the framework of the LCA methodology proved invaluable in reporting findings useful to the technology developers. Providing the entire life cycle, in which they might only play a certain part, highlighting the elements within and outside of the technology developer's control allowed for a more targeted feedback for further process development, as per the discussed framework in chapter 3.

In addition to assessing the processes based on the measured performances of the specified materials developed, the implications of an ideal performing material (i.e. maximum conversion of CO_2 under the assessed conditions) allowed for more informative instructions and targets for development, than a meaningless "make it better" feedback. Since, in addition to process-specific impacts, the use of LCA provided a much wider account of the hurdles (in addition to outright ENM material function) that require addressing before the entire technology solution becomes an

environmentally competitive package; both in comparison to existing industrial pathways across the range of impact categories assessed, and in the context of CCU performance net CO_2 abatement impacts.

8.7.1 *OPERATIONAL LIFETIME*

The operation of the assessed RWGS-FT and Electrochemical routes in the previous section 8.6 were stated for pre-defined, although deemed sensible approximations, for a 5,000 hour catalyst lifetime and 30 year infrastructure plant lifetime.

As a means of being more informative to technology developers, lifetime targets were set for the catalyst and total system installation payback periods. This latter measure represents the time duration of operation before net-negative GHG, and other impacts are offset. GHG break-even points are reached in approximately 7 years for RWGS-FT with iron-palladium, and much shorter for the electrochemical route of within a year. With consideration of the GHG payback period of the ENM catalysts alone:

- Fe40Pd1 0.08 years,
- Fe@CNT 0.06 – 0.10 years (dependent on whether ambient or high pressure)
- CS1 0.21 years,

Therefore although as an overall system the RWGS-FT has more capital equipment associated with its operation, in terms of active materials it is performing more favourably. This means the CS1 electrode coating is expected to perform at significantly longer, currently unproven, periods of operation than the other technology counterparts.

8.7.2 *TECHNOLOGY SCALES*

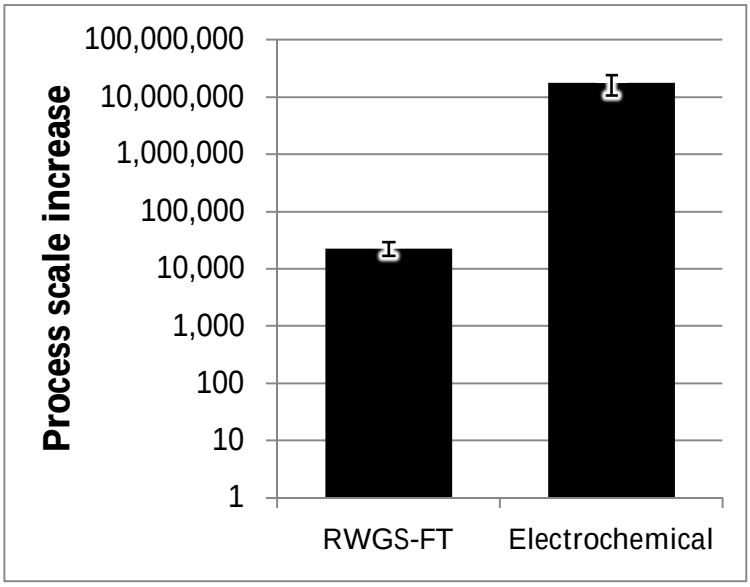


Figure 8-3 Process scale increase for conversion of 1kgCO_2/hr

The masses of products being formed by the laboratory processes are very small; for the RWGS-FT milligrams per hour, and electrochemical process are in micrograms per hour. Present setups are in developmental stages, exploring catalytic process activity and selection of best ENMs, and not concerned with the conversion of large quantities of CO_2. With reference to Figure 8-3, the processes would have to be greatly scaled up in order to produce even modest CO_2 conversions of one kilogram per hour. This conversion rate would result in extracted carbonaceous products in the region of hundreds of grams per hour, appreciably still significantly less than the scales of traditional refinery and the societal demand for the products.

Due to the means in which the LCAs have been conducted, especially with consideration of lean setups and industrially relevant co-produt exploitation, the inherent operational impacts are likely to remain proportionally similar. At the very least, the LCA work will act as a guiding blueprint for the aspects within the systems that carry more incumbent environmental burdens.

8.8 WIDER ENVIRONMENTAL IMPACTS

Table 8-3 Relative environmental performance between best case technologies in converting 1 kg of CO_2

	RWGS-FT		Electrochem
	Fe40Pd1	Fe@CNT -2.5bar	CS1
Climate change CO_2 eq.	***-1.15 kg***	***-1.07 kg***	***-1.30 kg***
Climate change	**2**	**3**	**1**
Ozone depletion	*3*	**2**	**1**
Human toxicity	*2*	*1*	*3*
Photochemical oxidant formation	*3*	*1*	*2*
Particulate matter formation	*3*	*1*	*2*
Ionising radiation	*2*	*3*	**1**
Terrestrial acidification	*3*	*1*	*2*
Freshwater eutrophication	*2*	*1*	*3*
Marine eutrophication	*1*	*2*	*3*
Terrestrial ecotoxicity	*3*	*2*	**1**
Freshwater ecotoxicity	*2*	*1*	*3*
Marine ecotoxicity	*2*	*1*	*3*
Agricultural land occupation	*2*	*3*	**1**
Urban land occupation	*2*	*1*	3
Natural land transformation	**2**	**3**	**1**
Water depletion	*2*	*3*	1
Metal depletion	*1*	*2*	*3*
Fossil depletion	**2**	**3**	**1**
Cumulative Energy Demand	**1**	**2**	*3*

Rank: 1 = best, 3 = worst of assessed technologies.

Boxed, underlined and bold numbers refer to conditions where environmental offsets are being achieved in the respective impact categories.

Throughout this thesis a discussion of a wider potential environmental impacts, based on the ReCiPe midpoint and cumulative energy demand methodologies. This has often brought to the fore many findings that would have gone unnoticed if carbon foot printing, or greenhouse gas impacts, were to be considered in isolation. Many of these have already been discussed in this chapter.

Within chapter 6 and chapter 7 it is shown that potential GHG net beneficial impacts are hypothetically achievable, however few other environmental benefits are seen for the operating system. This is summarised and compared across technologies in Table 8-3;

providing an overview of the best case scenarios of the best performing ENM-based processes. On the whole the electrochemical route can be considered more offsetting than the other two routes, managing to translate a unit of captured CO_2 into a greater net life cycle offset, additionally the electrochemical route is able to achieve more impacts with an overall negative offset. However, as stated previously this is reliant on the potential offset achieved by the type of products being performed, rather than the operational performance itself being environmentally negative in its operation.

8.9 OTHER CASE STUDY LCA LIMITATIONS AND FINAL THOUGHTS

With a wider consideration of limitations of the methods and approaches used in this thesis.

8.9.1 *APPLICATION OF LCA*

LCA does not consider local effects, but instead considers more global potential impacts that arise from the life cycle of a product or system. Since GHG impacts will be part of a global environmental mechanism it can be said with some certainty that these are likely to remain faithful to the results reported within this thesis. However, impacts which are spatially influenced such as potential release of toxins into different environmental compartments are indicative and not necessarily a fair representation to the environmental impacts of the specific systems under investigation. Further environmental risk assessment work would be advisable if and when technologies reach larger scales of production in which decisions over supply chains of resources, and full waste treatment practices are to be implemented.

LCA data will gain more certainty when applied to a pilot-scale and more industrialised pathway. Process inventory work as it presently stands has not assessed a fully-deployable system. Although the major components, identified as necessary for both the synthesis and the operation of ENMs in CCU applications, have been captured. There remain unassessed activities, these include likely filtration and separation stages. For example, extraction of unreacted feedstocks from formed products for effective process re-use, and further separation of formed products into single-product streams.

The debates of whether to pursue certain technologies are further aided with quantitative metrics of assessment. However, understanding the background nature of these values and an appreciation of the inter-play of factors are of greater importance and insight than the absolute values alone. Indeed, it would be unwise to quote any absolute LCA 'figure' without understanding or appreciation of how this number came about. It is for this reason that the boundaries, assumptions and contents of the LCA findings require transparent reporting; an endeavor throughout this thesis and affiliated publications

8.9.2 *DATA GATHERING*

LCA work is one where is easiest applied retrospectively to processes, as highlighted in the methodology section, and (Hetherington et al). At this point data is more available, not only on the functional performance of a system, but also in a more firm perspective with regard to the likely final materials and processes in place to fulfil these functions. However, with these limitations and arguably failings, where the process did work it did so in a very positive way, and has formed the basis and part-framework for further development in the promising CO_2 converting technologies.

Many potential ENM types and compositions exist. This proves a challenge for the LCA practitioner to keep abreast of these, and work at pace to feedback key data on promising material back to the technology developers. The dependency of the LCA process on the progress of other research groups proved a major stalling point in the inventory gathering stage. As is common practice in material science, researchers cast wide nets when in the explorative stages of identifying materials to meet certain functions. Often these materials did not prove fruitful in terms of performing CO_2 chemistry, and thus work would start afresh on alternatives.

Although masses of inventory data remain ripe for gathering across the laboratories of the collaborators involved in the LCA process, and moreover in the numerous other international research departments exploring ENM material synthesis and applications, it would be too wide a scope to detail every method covered. In keeping with the scope and unifying question of this thesis, interpretable as "identifying the potential role ENMs might have in CCU applications", and thus only materials which have demonstrated the potential for CO_2 conversion are assessed in this thesis.

Chapter 9: CONCLUSIONS, RECOMMENDATIONS AND FURTHER WORK

"a fo ben bid bont"
Welsh Proverb, ~in order to lead, you need to be a bridge.

This thesis spans many areas of current science and engineering research. The findings are laid out to bridge gaps between disciplines, in the immediate sense to establish firm dialogue between those involved with technology development for environmentally remediating objectives.

This research was needed to gain insight into engineered nanomaterials (ENM) converting CO_2 into higher value compounds; these fall under the umbrella term of carbon capture and utilisation (CCU) technologies. The purpose of CCU is to mitigate the associated climate change impacts of CO_2 release, providing a driver for its capture. Furthermore, the use of CO_2 as a feedstock chemical offers an alternative route in the production of fuels and chemicals; de-coupled from present dependency on fossil fuels, and void of current geological, and geo-political boundaries. Our dependency on hydrocarbons as transport fuels and other vital chemical industries is likely to continue for many decades before meaningful uptake of alternative sources occurs. CCU can be seen as a bridging option, maximising the return of extractable resources from our finite fossil fuel reserves, and begin the journey towards more sustainable fuels and chemicals. Technology developers are of course aware of these objectives, but are often detached from appreciating the wider environmental performance of their investigated systems.

The life cycle assessment (LCA) environmental management tool was used as the primary means of evaluating the different materials and processes being developed for the CCU routes investigated. LCA allowed the attributing factors behind the potential environmental impact of the systems to be investigated. This thesis treads in, and aims to contribute to, recognised areas of uncertainty within the LCA, namely the:

- assessment of ENM synthesis,
- provision of early state emerging technology assessment,
- quantitative accounting of carbon capture and utilisation technology solutions.

The case studies assessed, offer quantitative examples of how LCA can deliver findings to better equip technology developers and decision makers to the 'true environmental costs' of processes. Forming arguments and strategies for the uptake of complex solutions require more than speculation, and the LCA process affords a weight of qualitative and quantitative outputs to facilitate these. Systematic approaches, such as those employed and exemplified during the course of this thesis, are always preferable when so many factors are at work in a holistic system.

Processes that make use of CO_2 often follow with statements related to 'carbon neutrality'. However, often these results ignore, not wholly account or fail to report on the nature of the full life cycle of such processes; making the determination of whether net reduction in atmospheric GHG difficult to confirm. In this thesis a transparent account of the use of CO_2 throughout the life cycle is undertaken allowing the appreciation of any net GHG benefits; and other incurred environmental impacts that arise along the CCU life cycle.

9.1 CONTRIBUTION FROM THIS RESEARCH

Aim: ***Provide a more quantitative understanding of the potential benefits, in terms of mitigating climate change and other environmental impacts, to guide those wishing to use nanotechnology solutions for the conversion of CO_2 into commodity products.***

The research aim for this work was addressed by meeting four objectives. The following sections conclude on how these have been achieved in this thesis.

9.2 ESTABLISH THE ENVIRONMENTAL IMPACTS OF FORMING THE NANOMATERIALS

Bespoke datasets have been created for a number of ENMs. These are contained within chapters 4, 5 and 7 of this thesis, covering multi-walled carbon nanotubes, nano iron with palladium on silica substrates, and nano gold with palladium shells deposited onto carbon black.

A detailed capture of the direct and upstream life cycle activities allowed for the environmental footprint of these materials to be established. MWCNTs have seen the most LCA interest; however, these assessments were found missing in terms of accounting for an actual characterised materials. This LCA work provided further insight than previous nanotube studies: providing environmental indicators in addition to climate change and consumed energy. The MWNCT LCA results also have fuller coverage with respect to the relative feedstocks, direct process measurements and end-of-life treatments; chapter 4 details this LCA work; which is an expansion on the author's related publication (Griffiths *et al.* 2013a). With regard to the nanometal deposited materials in chapter 5 (published in Griffiths *et al.* (2013b)) and 7, to the author's knowledge no LCA coverage of these materials, or similar, have been previously conducted to date. Therefore, these findings lay benchmarks and early insights into the impacts of forming such materials.

In addition to providing the environmental footprint of the formed ENMs, the disaggregate nature of the collected inventory datasets allowed the intrinsic impacts and those that could be potentially mitigated to be appreciated. Through a series of conservative modelling approaches, it is apparent that significant impact reductions could be achieved. All ENMs assessed were energy intensive in their nature thus show preferential benefits once process move towards continuous from batch synthesis procedures. Energy impacts were particularly dominant overall from the perspective of climate change, fossil reserves, and energy consumption impacts; these are all significantly reduced once renewable electricity sources are considered.

When considering ENMs composed of precious metals, the high impacts of metal use are dominant in approximately half of the assessed 19 impact categories (ReCiPe midpoint indicators with the cumulative energy demand methodology, detailed in chapter 2 of this thesis). The nano exploitation of these precious materials is close to representing their maximum functional yield, therefore no reduction in the materials can occur without affecting the catalytic performance. It therefore followed that the only way of reducing these impacts requires more technical intervention at the end of their service lives. The LCA work explores a hypothetical metal recovery stage, to recoup the precious reserves and return them into the technosphere. Benefits of metal recovery are

apparent in the categories where metal use are dominant, however an increase is potentially witnessed in other environmental categories; unless a renewable electricity source can be used.

The LCA work of these modelled scenarios has presented technology developers with the most representative indication of ENM gate impacts at more industrial stages, armed with this information at such an early and developmental stage of process design phase will be beneficial as the technology advances into more pilot-scale synthesis processes.

9.2.1 *ESTABLISH THE LIFE CYCLE IMPACTS OF THE DEVELOPED CCU PROCESSES, AND REPORT ON THE ENVIRONMENTAL FEASIBILITY OF FURTHER TECHNOLOGY DEVELOPMENT*

The LCA work of this thesis represents the first in the field of CO_2 conversion via a reverse water-gas shift combined Fischer-Tropsch (RWGS) (Griffiths *et al.* 2013b) and electrochemical reduction pathways. The findings are thus of interest to many investigating the environmental performance and feasibility of emerging CCU technologies.

Similar to the capture of ENM synthesis impacts, the operation of the ENMs within their respective CCU processes was assessed to a high level of process detail. Within the confines of the operating process the different ENM material sub-types were assessed from a full life cycle perspective. The gate impacts of ENM material synthesis, were assessed in relation to the in-use performance and achievable environmental offsets, the result of which allowed for quantitative comparison to be drawn in the selection of best overall performing materials.

Processes were converting CO_2 destined for atmospheric release into carbonaceous compounds with market value. The LCA work accounts for the GHG impact of CO_2 throughout the assessed systems to validate whether any net climate change benefits would be achieved. Moreover, the resultant identified (or predicted in the case of electrochemical chapter 7) formed products are compared with the impacts of forming them via existing, typically crude-oil and fossil fuel pathways. Therefore establishing

whether environmental benefits can be seen for supplying the products via these alternative ENM-based CCU processes.

At the laboratory technology scale all assessed processes were unable to operate within GHG neutral or negative envelopes, nor indeed form carbonaceous products at a lower impact to that of traditional routes.

Processes at the laboratory scale were confirmed as being incumbent with poor thermal efficiencies, non-direct auxiliary devices, and high material and capital equipment infrastructures with relation to the low throughput of formed products. All of these attributing factors cloak the potential performance of the CCU processes, and thus the LCA model was interrogated for areas were process improvement potential existed.

Reduction of laboratory inefficiencies proved significant in minimising the net impact of the CCU technologies. However, significant improvements were only achieved once wider system changes were considered. The electrochemical process is dependent on renewable electricity operation, but of equal necessity is recovery of precious metal content of the active electrodes retrieved after their service lifetime. The best case modelled scenarios shows that there will inevitably be a GHG impact associated with the operation, however, the lowering in carbon intensity of the process can potentially result in products of a lesser carbon footprint in comparison to existing processes.

The assessed RWGS-FT would not be environmentally feasible when powered by any conventional energy source. However, industrial scale Fischer-Tropsch plants require cooling during operation, since at these scales the exothermic nature of the conversion process is apparent; indeed without intervention excessive heat release would cause thermal overrun of plant reactor. Thus, with realisable heat extraction the process ceases to be energy demanding to energy supplying; which dramatically improves its net environmental performance and feasibility.

Based on actual performance of the respective CCU processes, and the expectation that heat provision can be harnessed the operation of the RWGS-FT can occur with a net GHG benefit, products are thus less impactful than traditional routes, or in the best foreseeable cases as carbon sinks; i.e. net negative hydrocarbon products. These findings are significant since they are founded on a comprehensive grasp of the upstream

embodied impacts associated with system, not only in terms of in-use perceived performance, but net life cycle sequestration/offset of CO_2 is achievable.

9.2.1.1 Technical lifetimes

In meeting environmentally beneficial operations, sustained use of the ENMs, and indeed capital equipment is required. Presenting results for the assessed CCU routes have found that the materials must exceed their current tested performance times whilst maintaining their measured conversion rates for many months of continual operation.

If these conditions can be technically met then the ENMs would be able to not only offset their own incumbent impacts, but providing an alternative source of valuable fuels and chemical compounds at a lower environmental impact than what society is presently 'paying'.

9.2.2 *COMMUNICATE TO TECHNOLOGY DEVELOPERS KEY LIFE CYCLE RESULTS FOR ACTION*

Further to the identifying of inherent impacts of the operating processes, meaningful change and process improvement can only occur through targeted action. In light of this the presentation of findings to specific researcher groups were presented in terms of the activities which are within and outside of their immediate control.

Relative ENM life cycle impact performance was presented separate from the capital equipment, in this way the net life cycle performance of catalysts, and full system could be established. This separation allowed for an appreciation of whether the processes would ever be environmentally feasible, or being held back by -arguably unrepresentative- laboratory practices and inefficiencies.

In order to provide technology developers with a performance target for their developed materials, idealised reaction performances were hypothesised. To this end, the complete conversion of CO_2 into products was considered, with the formed product mixes representing an ideal output in terms of selectivity towards more valuable and inherently impactful materials typically sourced fossil fuels. This provided the best case scenario in terms of obtainable in-reaction environmental offsets, and more importantly the proximity in which the materials were from reaching these targets.

Although exact process design is not determined for the assessed routes, the LCA work provides an account of the relative intensity of an operating plant that would be necessary for environmental net benefits to be achieved. This is a significant consideration when scaling the processes to more industrial levels of operation.

In addition to quantitative results, much of the LCA feedback to technology developers occurred via qualitative means. This is appreciably harder to measure, however, collaborators involved throughout this research became ever more understanding of the breadth and depth of process considerations that needed to be accounted for in addition to the in-situ reaction performance of tested materials. The provision of system boundary diagrams and capture of relative impacts of upstream materials were of great interest and considered as very informative for their work, appreciating where their system choices could be changed for future process advancement.

9.2.3 *COMMUNICATE WIDER LIFE CYCLE ENVIRONMENTAL IMPACTS*

The accounting of net CO_2 life cycle offsets and associated GHG impacts was the primary focus of the developed technologies. If processes are not achieving beneficial climate change performances then there would be no environmental justification or purpose in their operation. Once processes, through models and hypothesised scenarios, indicated favourable net GHG impacts then other environmental impacts were explored.

The effect of GHGs on climate change is one of many environmental mechanisms in which human activity is measurable. LCA offers insight into many more elements in which operating processes and their associated activities might potentially have on human health and the wider biosphere. The potential effects stem from: the release of toxins and excess nutrients, ozone depleting, radiation, particulate matter; and indeed coverage of the likely land use, and quantified consumption of fossil fuel and mineral ore reserves.

The output of this work have been characterised impacts the across multiple environmental categories, for both ENMs formed and operating CCU processes. Although such impacts are largely to be treated as indicative accounts, since the exact impacts of such environmental effects would require site-specific risk assessments, they

provide a basis for comparison between technologies. Moreover, the consideration of wider environmental impacts provides an indication of the inherent impacts, and those which could be potentially offset, through the operation of the different ENM-CCU processes. Through drawing direct comparison with existing methods of carbonaceous product formation, e.g. crude oil refinery, environmental payback periods across the different assessed impacts were calculated. Cases where no potential for environmental payback are also highlighted.

The findings show that although there are theoretical, arguably practicable, means of reaching net GHG performance levels, resulting penalties arise in other assessed environmental impacts such as toxicity, eutrophication and depletion of metal resources. Presentation of wider impacts ensures technology developers are made aware of the implications of mitigating one environmental impact at the cost, perhaps significantly so, of others. Arming decision makers with these findings presents quantitative basis for technologies to be operated, and guide process designers on developing solutions that consider wider environmental receptors.

Within this thesis, cumulative energy demand, and the use of precious materials and associated impacts have significant bearings on the overall technology-specific recommendations. These would not have been realised or brought to the fore if carbon foot printing were the only impact assessment methodology being considered.

High energy intensity, consumption of precious finite resources, uncertainty over life cycle release points and resultant environmental impacts, and end-of-life treatment practices are concerns facing the adoption of ENMs. Additionally, benefits are not wholly recognised in the context of real applications for the ENMs to fulfil. This thesis has provided answers, albeit in targeted material groups and applications, for many of these areas.

9.3 RECOMMENDATIONS

Recommendations can be drawn from the absolute LCIA findings, and the wider methodological approaches and models used throughout this research.

9.3.1 *TECHNOLOGY DEVELOPER*

- Validation of continual process operation. Much of the identified benefits of the processes are only achieved for extended, months rather than current hours, periods of operation. Increased process runs times or simulation of longer in-situ lifetimes is necessary to establish whether changes or degradation occur in catalytic performance.

- The ENM synthesis and deposition should be mindful of end-of-life recycling and material recovery. Many of the whole life cycle benefits are only achieved once EOL activities are considered. Furthermore, the validation of EOL models used in this thesis with in-use empirically derived data in terms of extractable material content.

- The LCA work should continue to play a part, at least in some guiding form, as the technology progresses through different stages of development. Changes to the system need to be captured to assess life cycle performance effects.

- Pursue all assessed options. Initial findings suggest benefits are achievable at larger process scales. The next stages should consider the implementation of industrially-representative setups to validate expected benefits and co-product exploitation which are likely with increasing scales.

9.3.2 *FUNDING BODIES AND POLICY MAKERS*

In addition to academic output, the results of this thesis will be information to wider investors and industrial parties. It is foreseeable that these emerging technologies will carve an industry for themselves, however, this will be dependent on wider factors. Global drivers in the reduction of national GHG emissions either through political pressure or changes in taxation of emissions, could lead to an increased impetus to

prevent CO_2 emissions. The prospect therefore of technologies that can use this waste feedstock becomes an attractive avenue for investigation.

Specific recommendations for those considering CCU technologies to mitigate GHG impacts or indeed seek to use CO_2 as a feedstock rather than waste, are that:

- This is the early stage of the development, however, in the case of RWGS-FT catalysis processes there are promising early findings demonstrative of a solution which could reduce net operating GHG emissions.

- These technologies at their present scales do not offer "off the shelf" solutions, however, on the basis of early scoping and forecasting work, both RWGS-FT and electrochemical CO_2 conversion routes have the potential to offer environmental returns within the order of a decade of operation, and potentially shorter periods for the best cases.

- Investors with moderate supplies of CO_2, and additional access to waste heat might benefit from small to medium scale technology packages. Those with larger sources of CO_2, and committed to larger capital investment, might well see CO_2 mitigation, product formation and the co-generation of energy. The technologies could be considered as potentially being able to piggy-back off existing processes. Especially those in mass scale enterprises such as the chlorine industry, where CO_2 from electricity generation and H_2 are both (largely) unused co-products of the industry.

- It would be recommended that these technologies are kept in mind in the context of future economic, environmental and social changes. The price of crude oil and other hydrocarbon sources of the future, and indeed a more strongly incentivised carbon tax system, might well make alternative routes such as those within these thesis attractive options to pursue.

- Recommendation that a review board conduct targeted studies on emerging materials and technologies which have shown promising performances in a given application. Recognition of this could be from findings which have attracted significant academic citations, or received external funding to bring the

technology through pilot-scale. This way LCA efforts are prioritised for the coverage of ENMs being rolled out

- The roll-out of ENMs should occur in parallel to the advancement of adequate end-of-life strategies in place for the retrieval of precious metals and other materials. To not only reduce the environmental impacts of their use, but to mitigate the potential risks posed by presently uncharacterised materials in the natural environment.

9.4 FUTURE WORK

Due to the nature of the work contained in this thesis, many avenues for further pursuit and potential off-shoot studies can be identified. In the first instance, it would be highly desirable to continue with the assessment of processes subsequently developed by the collaborators of this work. Many came to light late into this research, and are indeed still being generated by the research groups within the University of Bath, and the University of Bristol respectively. In addition to continuing LCA input for these processes, activities for further related work could also include:

- The assessment of more materials. As demonstrated in this thesis, the incumbent life cycle impacts are distinct for the material class being covered. More work on ENMs, both similar and different will allow for a more meaningful account of root-cause impacts. The output of which could be considered a database, and/or predictive tool, in which users define a material by its properties, and this produces a likely environmental impact.

- Conducting a more detailed market assessment of the likely penetration, uptake and demand for the products being formed. Environmental criteria, although informative in the comparative offset being achieved, are only part of the criteria in which technologies must meet in order to be considered attractive technologies worthy of further pursuit.

- The life cycle costing of options would be a natural follow-on from the work contained in this thesis. The system boundaries are defined and material inventories are broadly in place, thus a considerable portion of the foundation

work for costing has been conducted. Economic analysis would provide a valuable and complimentary addition to the fuller appreciation and debate over the pursuit of these early-stage processes.

- Conduct a more accurate account of CO_2 capture and delivery to point of use. CO_2 feedstock impacts within this thesis are first-approximation figures, awaiting more detail from established and empirically derived data sources. Furthermore, to align the results of this study with air-capture technologies of CO_2, i.e. those capable of extracting CO_2 from the atmosphere rather than point-source emitters.

- To expand the scope of the LCA work to validate the findings with different energy and feedstock sources. Electricity impacts were amongst the most dominant, and thus considering different specific mixes other than those of the UK and a sole wind generation model would provide a more balanced account of operating impacts. The integration of future electricity scenario mixes might also be beneficial, such as to determine if likely future de-carbonisation of the electricity network make the operation of these processes viable.

- Produce chemical process/plant models of large scale systems based on the laboratory processes; validate the relative impacts of capital infrastructure, obtainable process heat, and achievable yield and plant capacities.

- Explore where these technologies could be incorporated within wider technological systems. This could be considered as a direct bolt-on technology potential for utilising CO_2 from point source emitters, streamlining the overall processes. Furthermore, there is a large unexplored potential to couple the assessed processes with other technologies and systems, such as renewable energy generators during periods of low grid demand, or waste heat for small-scale RWGS-FT reactors.

9.5 CLOSING REMARKS

This thesis has shown that a process in its very early stages of development can be interrogated, assessed and compared on a functionally equivalent basis to long established and proven technologies. Albeit without a rigid framework, the approach shows a means of separating the many elements present in early process into factors which can be mitigated to those which are inherent in the functional performance of the system. Such insight allows an overall appreciation of likely pitfalls and incumbent burdens in which a system will carry through further stages of pilot-scale and more industrialised roll out. Furthermore, it allows the early evaluation of other potential processes which might be plagued by unsurmountable incumbent impacts, and thus never capable of achieving environmentally beneficial performances.

The findings, although presently for only a small sample of known and ever-expanding ENMs, are indicating of both the similarities and key differences between this specific class of materials. Although grouped as one class “ENMs” they cover a very broad range of synthesis activities, only a small sample have been covered in this thesis, however the outcome of these findings underline the need for trunk datasets to be produced. Datasets which account for common nano-dispersion, growth, and other synthesis techniques, from these materials and process parameters could be included to produce streamlined LCA. Since once the core routes of the material synthesise were appreciated in this thesis, the composition of different metal loadings led to the discrepancies between separate yet related materials.

The raw potential of many ENMs are currently being hidden by the inefficiencies and process specific burdens at the laboratory scale. Many of the ENMs are performing at very favourable conditions compared to referenced ‘ideal’ conversions, although far from optimised, they show that process design is the next avenue of investigation. The need for a more industrially representative pilot scale is needed to assess the feasibility of further advancement of these CCU technology solutions.

The work contained within this thesis has contributed to the wider LCA fields, adding more inventory data for others to use. Furthermore providing fundamental insight into novel processes being developed to meet the very real challenge of mitigating

anthropometric climate change. LCA has reaffirmed expected high burden activities but provide a quantitative and relative account in the context of all contribution system flows. Moreover, the use of a life cycle thinking approach has cast new insight into the potential to reduce impacts, appreciating the factors in which technology developers can take ownership and control over.

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APPENDIX A: RESEARCH BACKGROUND

The Engineering and Physical Sciences Research Council (EPSRC) funded projects '*addressing societal and/or economic issues where nanotechnology can make a unique and significant contribution*'(EPSRC 2009). In meeting these objectives the EPSRC framed a series of Nanotechnology Grand Challenges (NGC), to date these include:

- 1st Energy (started in 2008)
- 2nd Healthcare (started in 2009)
- 3rd Environment (started in 2010); this thesis sits within deliverables

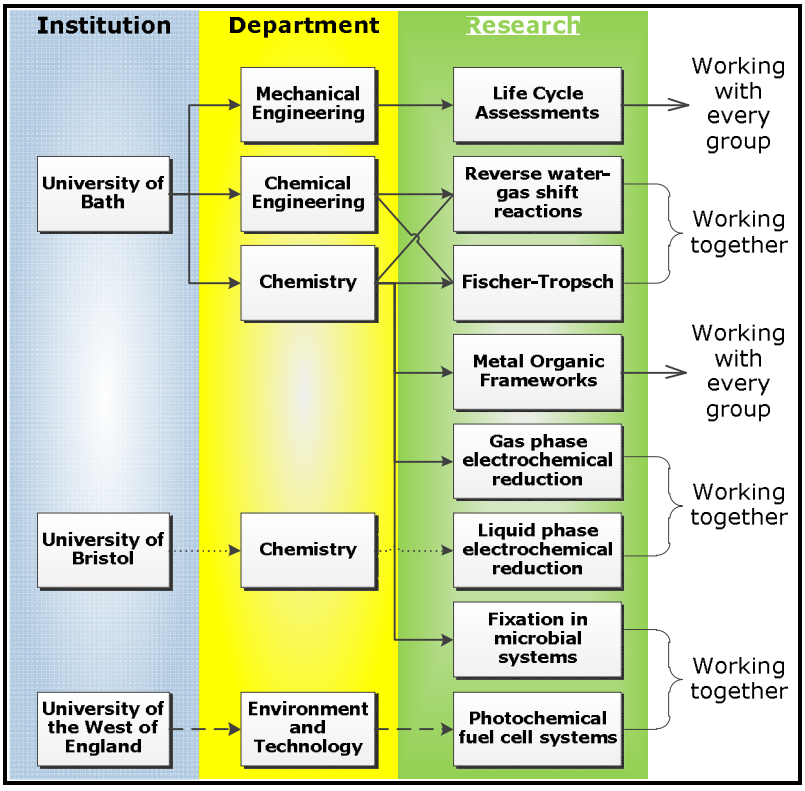


Figure A-1 Organisational structure of the NGC team, knowledge transfer will occur between all research groups.

The work contained in this thesis is funded and founded upon the Environment third NGC "seeking proposals that address the contribution which nanotechnology can make to Carbon Capture and Utilisation". In so doing a team of researchers from the University of Bath, University of Bristol, and the University of the West of England collaborated in the development or advancement of nanomaterials for CCU, as shown in Figure A-1. To varying extents groups worked together to mutually advance their research.

APPENDIX B: BACKGROUND DATA FOR ELECTRICITY AND HYDROGEN DATASETS

All equipment and processes assessed in this thesis derived their power from electricity, their impacts are directly associated to the source nature of the generation mix. As chapter 3 states, the difference between coal and gas emissions are considerable; GHG emissions three-fold that of natural gas. Appreciating the UK grid mix to be a product of a combination of fossil fuel and renewable generators the electricity impact is a mean value of each generation technology's proportional impact, as outlined in Table 8-4.

Table 8-4 Datasets chosen to represent UK electricity mix. With breakdowns of respective relative contribution towards final generation and GHG emissions respectively, based off 2009 UK generation data, (DUKES 2011)

Source	% Generation	% GWP
Electricity, natural gas, at power plant/GB U	**43.7%**	**39.2%**
Electricity, hard coal, at power plant/UCTE U	**27.6%**	**55.3%**
Electricity, nuclear, at power plant/UCTE U	**18.3%**	**0.3%**
Electricity, at wind power plant/RER U	**2.5%**	**0.1%**
Electricity, hydropower, at power plant/GB U	**1.4%**	**0.0%**
Electricity, biogas, allocation (…) 180kWe, future/CH U	**1.3%**	**0.7%**
Electricity, oil, at power plant/GB U	**1.2%**	**2.5%**
Electricity, hydropower, at pumped storage power plant/GB U	**1.0%**	**1.6%**
Electricity mix/FR U	**0.8%**	**0.1%**
Electricity from waste, at municipal waste incineration plant/CH U	**0.6%**	**0.0%**
Electricity, production mix photovoltaic, at plant/GB U	**0.5%**	**0.1%**
Electricity, biomass, at power plant/US	**0.5%**	**0.0%**
Electricity, biowaste, at waste incineration plant, allocation price/CH U	**0.5%**	**0.1%**
Electricity, digester sludge, at incineration plant, future, alloc. price/CH U	**0.2%**	**0.1%**
Global warming potential impact ≈ 0.54 $kgCO_2eq$ / kWh_e		

The electricity data in this thesis has been fixed to the year 2009, i.e. the most recent data available when this research was first undertaken by the author (DUKES 2011). Since then data up to and including 2012 is available (DUKES 2013). The total consumption of electricity has not significantly changed over the past few years, although has continued in an incremental downward trend over the past 5 years, influenced by a slowing industrial sector. A significant switch, however, has happened with coal replacing

natural gas as the most dominant source of generation, this can be appreciated in Figure B-1.

The change in generation mix was largely attributable to the relative decrease in coal price, in the wake of US shale gas exploitation, and increase in natural gas price respectively. Renewable share has had the largest single relative shift, owing to increased offshore and onshore wind capacity and government financial incentives leading to a 'PV-boom'. When considering this shift, the life cycle impact of UK electricity generation has risen from the 0.54 to around 0.62 $kgCO_2eq$ / kWhe. The thesis has not been changed to reflect most recent values in order to keep consistence between thesis and its associated publications (Griffiths *et al.* 2013a; Griffiths *et al.* 2013b). Furthermore, the UK grid mix will very likely be different again by the time 2013, and 2014 data becomes available. Changing upstream data can be considered a challenge of using LCA. However, the changeable nature of the current hydrocarbon markets is a strength of CCU technologies, since the formation of commodity chemicals and fuels decoupled from market and political influence will

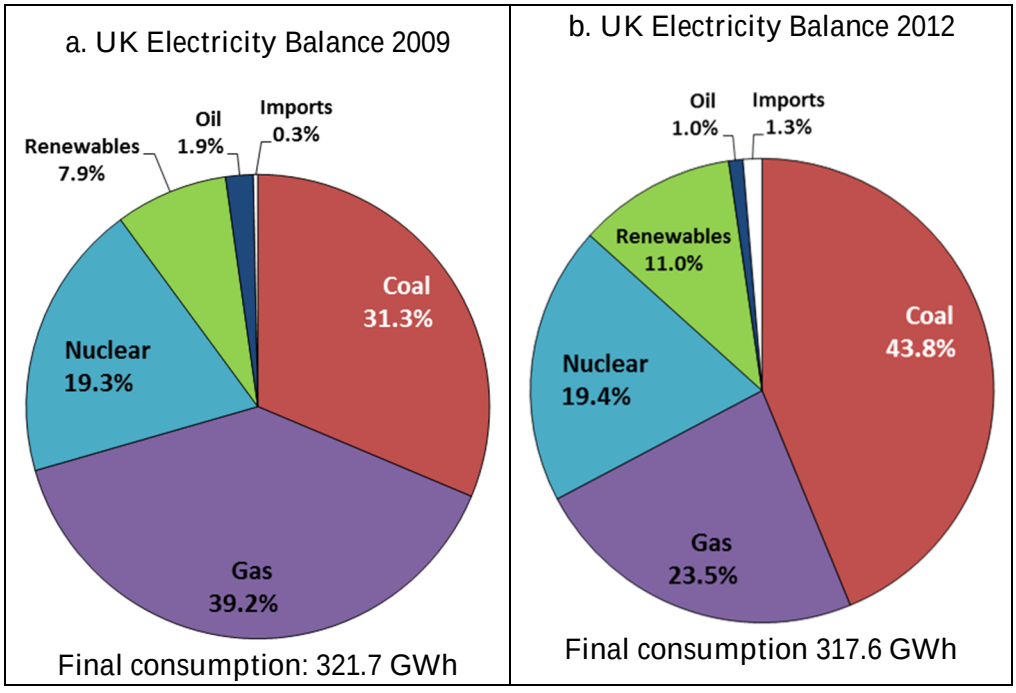


Figure B-1 The changing UK electricity mix between 2009 (data used in this thesis) and most recent figures 2012. Data adapted from: (DUKES 2011; DUKES 2013)7.

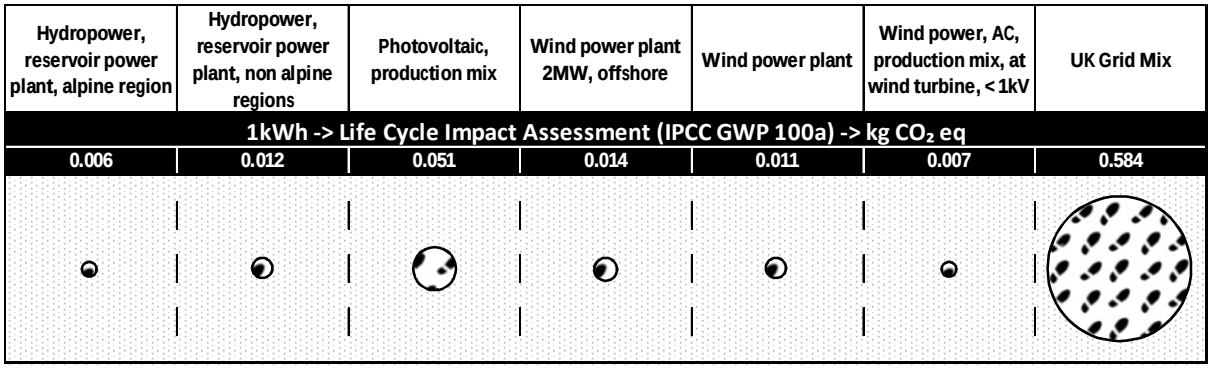
Appendix B.1 ALTERNATIVE ELECTRICITY GENERATION

The impacts of electricity, as demonstrated throughout this thesis, are the most dominant life cycle impacts for both the formation of nanomaterials and of the operating CCU technologies. It was felt necessary to demonstrate the effects of the electricity mix on the technologies being assessed, a strength of CCU technologies means that they're roll-out is potentially global, therefore fixating on the UK mix would provide a skewed account of potential performance, especially when considering the international range in grid mixes and resultant carbon intensities e.g. Sweden is > 95% hydropower resulting in 0.003 kg CO_2 /kWhe, where China, ~70 % coal, is 1.049 kg CO_2 /kWhe (Jager *et al.* 2005). From a life cycle perspective the use of lower emitting electricity sources will have an immediate and very impactful outcome on the overall performance of processes being assessed.

The dependency on the combustion of carbon-based fuels for electricity generation, subsequently used to power CO_2 conversion technologies for carbonaceous product formation is not a thermodynamically sound approach for successful CCU. In accordance to this, and as many report, there is a need to for renewable electricity to be powering these technologies. There are numerous political, financial and technical barriers to renewable energy exploitation. However, amidst these barriers are complimentary solutions to the exploitation of CCU, for instance the UK wind power infrastructure has now reached a level whereby during periods of low electricity demand and high wind speeds the electricity potential is curtailed, limiting performance of the installed turbines to lower their generation. Similarly with solar PV during sunny

[7] Differences between values quoted in Table 8-4 and Figure B-1 are due to statistical differences in the gathered data. "*These arise because data collected on production and supply do not match exactly with data collected on sales or consumption."DUKES (2011). Digest of United Kingdom Energy Statistics: Electricity.*. The table, based on table 5-1 in DUKES has a more accurate breakdown of individual electricity generators and is thus deemed more applicable in the formation of an attributional LCA suitable for modelling electricity use impact.

periods, dealing with these instantaneous peaks remains a challenge for the foreseeable future and various options for power-storage are being explored. Wind power generation is amongst the lowest established carbon sources available, and is a resource the UK is better placed than many in the world to best utilise.



A best case scenario grid mix has been taken, wherby the Ecoinvent data for a 'Wind power plant' has been used. The adoption of this dataset leads to significantly lower burdens from electricity usage, as shown in Figure B-2, and reported by others (Varun *et al.* 2009). An exception to improvements is seen for the metal depletion impacts, the increased infrastructure intensity and embodied materials in wind generation are above that of traditional fossil-fuel sources, the material impacts of turbine construction have been noted in other LCA assessments (Weinzettel *et al.* 2009), with recycling activities likely to decrease this amount, the determination of decommissioning impacts are subject to uncertainties and beyond the scope of this thesis work.

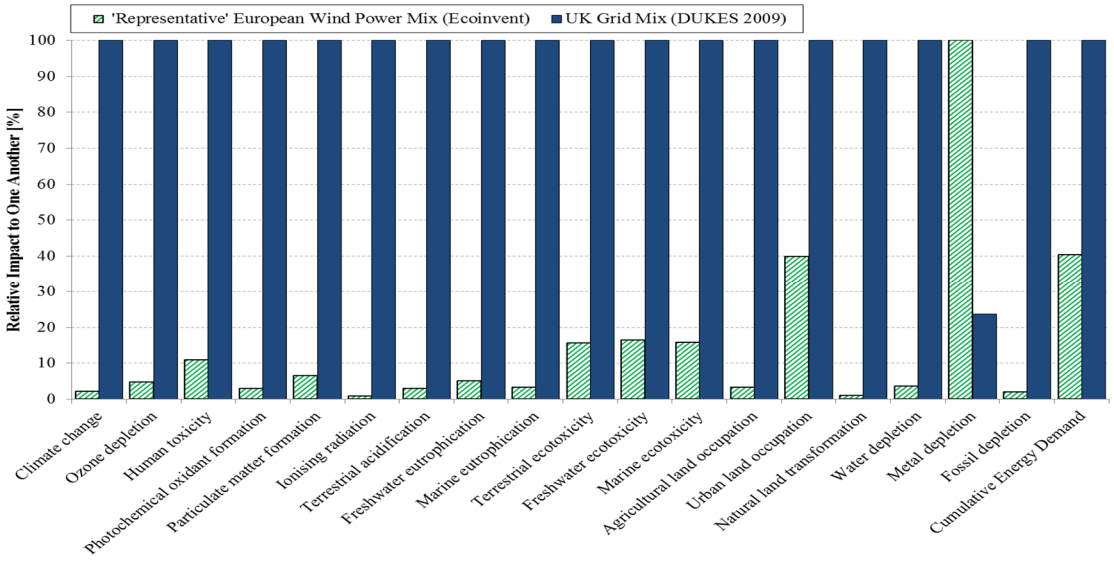


Figure B-2 Comparing impacts between modelled UK electricity grid mix, and electricity sourced from a 'representative EU' wind power site.

Quoting 'renewable electricity' impacts are arguably impacts far below even optimistic UK carbon targets, however, they provide an indicative account for what likely impact

Appendix B.2 HYDROGEN USE

A number of methods for hydrogen production exist from; established technologies, such as steam reforming, partial oxidation, electrolysis and biomass gasification, soon-to-be technologies; such as autothermal reforming, membrane electrolysers and ammonia reforming; towards the more experimental routes of microbial production and direct water splitting technologies via thermal and photoelectrical chemical water splitting technologies (Holladay *et al.* 2009). Although producing the same end-product, the impacts due to production of hydrogen, even via the most established production pathways differ greatly, as shown in Table B-5.

Table B-5 Global warming impacts from other LCA work of different hydrogen production routes.

Route of Hydrogen production	Specific global warming potential [$kgCO_2eq$ / kg H_2]
Natural gas reformation	**~ 7.8 (Plastics Europe 2011)** **~ 11.0 (Koroneos *et al.* 2004)** **~ 8.9 (Ruether *et al.* 2005)**

Coal gasification	**~ 12.4 (Ruether *et al.* 2005)**
Fossil fuel cracking	**~ 1.7‡ (Plastics Europe 2011)**
Electrolysis	**~ 1.0‡ (Plastics Europe 2011)**
Electrolysis via renewables	**~ 0.8 (Koroneos *et al.* 2004)** **~ 0.2‡ (adapted from (Plastics Europe 2011)**
	‡ datasets used in this thesis.

Three datasets for hydrogen production are used in this thesis. As can be appreciated from Table B-5, these represent the lowest reported impact for hydrogen production from fossil fuel and renewable electrolysis routes respectively. Other practitioners using the study results within this thesis should be mindful of this choice. Although the effects of H2 choice is measurable, they do not greatly influence the major findings and conclusions of the results detailed within this thesis. Justification for this choice is that the technologies themselves are established and commercially used technologies. In seeking to move towards larger-scale GHG mitigating impacts of deployed CCU technologies, system feedstocks would be sourced to minimise environmental burdens. Figure B-3 shows that trade-offs between hydrogen sources are occuring. Where as a 100% electrolysis route of H2 production is modelled as to de-couple this feedstock from fossil fuel origins, and thus associated GHG, fossil fuel reserves, and cumulative energy demand, it can be seen that other impacts are indeed greater for the chosen electrolysis-H_2.

The largest method of hydrogen production is via steam reformation of natural gas, it is the cheapest route (Crabtree *et al.* 2004) and uses natural gas as not only the feedstock but also the reaction energy source for production, however, it sits amongst the highest impact sources. The fossil fuel cracking route, is a pathway typically performed at a crude oil refinery, it is often a product liberated when splitting longer-chained hydrocarbons into shorter ones. The inventory data for the cracking route is representative of an industrial scale route and is detailed in the eco-profiles of feedstocks used by the European Plastics industry (Plastics Europe 2011). In keeping with a a representative global industrial pathways, consisting of 95 % from thermal cracking processes of fossil fuels, and the remaining 5 % from electrolysis (Häussinger *et al.* 2000; Kothari *et al.* 2008). The chosen Ecoinvent

(Ecoinvent Database v2.2 2010) incorporates the H_2 cracking, with 5% from chlorine electrolysis route.

The origin of the electrolysis route is founded on an Ecoinvent inventory report (Althaus *et al.* 2007), and is the co-product of a chlorine production cell. It has been allocated impacts on a per mass 46.4% chlorine, 52.3% sodium hydroxide, and 1.3% hydrogen, in accordance to the operation. The dataset is the author's own, in so much that it has been adapted so that energy is supplied via wind power generation, see previous section 0. , the use of renewable wind has been identified as a forerunner in terms of low-impact hydrogen production (Koroneos *et al.* 2004).

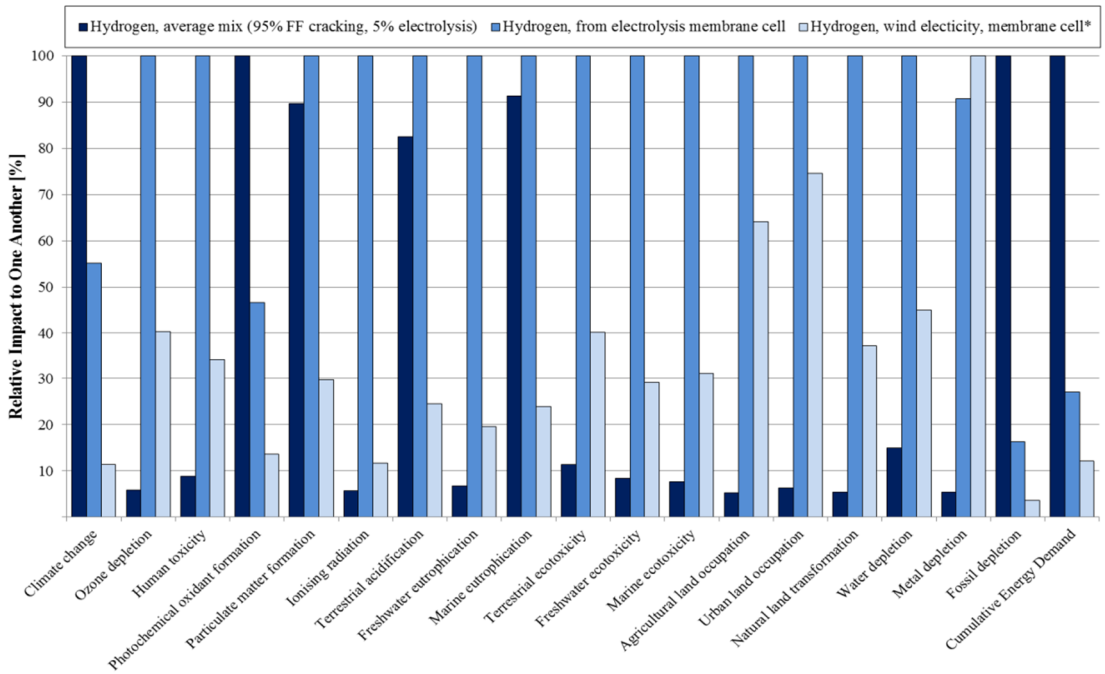


Figure B-3 Relative cross-category impact of the hydrogen datasets used in this thesis.

The choice of this particular membrane cell was made in the vision of using sea water, with the sodium chloride within it the necessary electrolyte. The co-products of chlorine and sodium hydroxide are non-trivial in terms of industrial application, and thus piggy-backing off these would allow for additional economic drivers in place of an electrolysis route which supplied hydrogen and oxygen alone from a cell requiring other electrolytes, such as potassium based. Furthermore, the chlorine industry in Europe is actively seeking ways to use this 'uneeded' hydrogen by-product from their industry(Euro Chlor 2011). This use of hydrogen viewed as a waste source, is in the similar vein to CO_2 use. However, the chlorine industry are also advancing research

into new lower-impact technologies that do not emit hydrogen (Jung *et al.* 2013), thus in the future the use of this hydrogen source might well have to be reviewed.

Table B-6 Impacts of hydrogen (1 kg) and electricity (1kWh) datasets used in thesis

Impact category	Unit	Hydrogen, liquid, at plant/	Hydrogen, RENEWABLE, liquid, membrane cell, at plant/	Electricity, production mix GB/ DUKES2009	Electricity, at wind power plant/
Climate change	kg CO2 eq	1.66E+00	1.89E-01	5.39E-01	1.12E-02
Ozone depletion	kg CFC-11 eq	3.42E-09	2.37E-08	1.52E-08	7.20E-10
Human toxicity	kg 1,4-DB eq	6.23E-02	2.39E-01	1.04E-01	1.13E-02
Photochemical oxidant formation	kg NMVOC	4.57E-03	6.20E-04	1.24E-03	3.58E-05
Particulate matter formation	kg PM10 eq	1.18E-03	3.93E-04	5.00E-04	3.22E-05
Ionising radiation	kg U235 eq	3.71E-02	7.59E-02	2.40E-01	1.96E-03
Terrestrial acidification	kg SO2 eq	3.28E-03	9.72E-04	1.61E-03	4.70E-05
Freshwater eutrophication	kg P eq	6.13E-05	1.76E-04	1.44E-04	7.23E-06
Marine eutrophication	kg N eq	8.41E-04	2.20E-04	3.98E-04	1.26E-05
Terrestrial ecotoxicity	kg 1,4-DB eq	1.07E-05	3.76E-05	8.94E-06	1.39E-06
Freshwater ecotoxicity	kg 1,4-DB eq	1.18E-03	4.08E-03	2.19E-03	3.58E-04
Marine ecotoxicity	kg 1,4-DB eq	1.07E-03	4.37E-03	2.39E-03	3.77E-04
Agricultural land occupation	m2a	1.41E-03	1.71E-02	6.71E-03	2.23E-04
Urban land occupation	m2a	3.42E-04	4.08E-03	2.19E-03	8.74E-04
Natural land transformation	m2	6.33E-06	4.41E-05	1.23E-04	1.21E-06
Water depletion	m3	1.92E-03	5.76E-03	3.08E-03	1.11E-04
Metal depletion	kg Fe eq	4.96E-03	9.24E-02	3.33E-03	1.41E-02
Fossil depletion	kg oil eq	1.62E+00	5.70E-02	1.75E-01	3.46E-03

‡Hydrogen, liquid, at plant – is an Ecoinvent dataset comprising 95% of hydrogen from fossil fuel cracking, and 5% from electrolysis of saline water. That is a representative mix for current H_2 production mixed.The fossil fuel cracking route data is based on data provided from Plastics Europe (Plastics Europe 2011)

APPENDIX C: SUPPORTING INFORMATION FOR CHAPTER 4.

Appendix C.1 ELECTRON MICROSCOPE IMAGE OF MWCNTS

Scanning electron microscopy (SEM) was carried out on a JEOL 6480LV at 5 - 20 kV, while high resolution SEM was carried out using a JEOL FESEM 6301F.

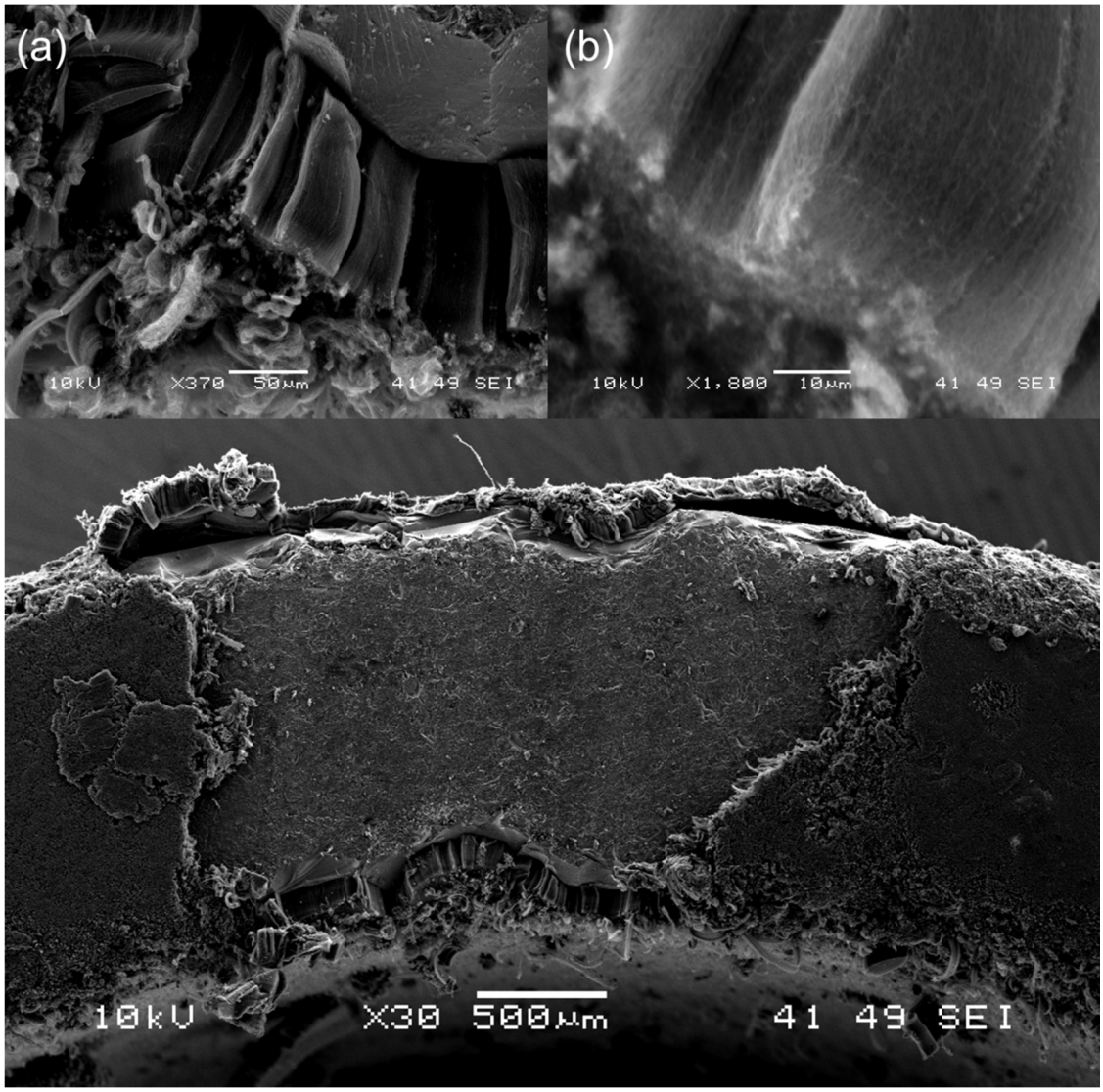


Figure C-4 Scanning electron microscope (SEM) image of deposited multi-walled carbon nanotubes (MWCNTs). *Note*: ordered and even deposition of the nanotubes grown, with consistent length in the order of 100 µm. Figure b. shows a highly magnified scan illustrating the aligned 'forest-like' nature of the MWCNT product.

Appendix C.2 FULL CHARACTERISED DATA

Method: Characterisation, ReCiPe Midpoint (H) V1.05 / Europe ReCiPe H

Chemical Impacts

Impact category	Unit	Ferrocene [0.2 g]	Toluene [8.67 g]	Argon *(heating)* [14.71 g]	Argon *(reaction)* [44.1 g]	Argon *(cooling)* [14.71 g]	Hydrogen [0.25 g]
Climate change	kg CO2 eq	2.70E-03	1.30E-02	4.61E-03	1.38E-02	4.61E-03	4.11E-04
Ozone depletion	kg CFC-11 eq	3.12E-10	2.37E-12	2.22E-10	6.65E-10	2.22E-10	8.45E-13
Human toxicity	kg 1,4-DB eq	1.03E-03	7.73E-05	2.93E-03	8.78E-03	2.93E-03	1.54E-05
Photochemical oxidant forma	kg NMVOC	1.24E-05	3.78E-05	9.69E-06	2.91E-05	9.69E-06	1.13E-06
Particulate matter formation	kg PM10 eq	1.30E-05	1.02E-05	6.00E-06	1.80E-05	6.00E-06	2.92E-07
Ionising radiation	kg U235 eq	7.48E-04	4.00E-06	3.55E-03	1.06E-02	3.55E-03	9.17E-06
Terrestrial acidification	kg SO2 eq	5.74E-05	2.98E-05	1.90E-05	5.69E-05	1.90E-05	8.11E-07
Freshwater eutrophication	kg P eq	1.04E-06	8.66E-08	4.46E-06	1.34E-05	4.46E-06	1.52E-08
Marine eutrophication	kg N eq	2.99E-06	7.02E-06	3.91E-06	1.17E-05	3.91E-06	2.08E-07
Terrestrial ecotoxicity	kg 1,4-DB eq	1.96E-07	1.35E-07	3.40E-07	1.02E-06	3.40E-07	2.64E-09
Freshwater ecotoxicity	kg 1,4-DB eq	1.88E-05	3.21E-06	6.30E-05	1.89E-04	6.30E-05	2.91E-07
Marine ecotoxicity	kg 1,4-DB eq	1.91E-05	4.17E-06	6.23E-05	1.87E-04	6.23E-05	2.65E-07
Agricultural land occupation	m2a	5.15E-05	2.09E-07	5.84E-05	1.75E-04	5.84E-05	3.50E-07
Urban land occupation	m2a	1.31E-05	4.29E-07	1.45E-05	4.34E-05	1.45E-05	8.45E-08
Natural land transformation	m2	6.12E-07	9.87E-11	4.85E-07	1.45E-06	4.85E-07	1.57E-09
Water depletion	m3	1.98E-04	9.05E-06	3.67E-05	1.10E-04	3.67E-05	4.74E-07
Metal depletion	kg Fe eq	2.04E-04	6.43E-06	5.96E-05	1.79E-04	5.96E-05	1.23E-06
Fossil depletion	kg oil eq	1.30E-03	1.28E-02	1.40E-03	4.20E-03	1.40E-03	4.00E-04

Electricity Consumption Impacts

Impact category	Unit	Furnace *(heating)*	Furnace *(reaction)*	Mechanical Syringe	Mass Flow Controller	Notes:
Climate change	kg CO2 eq	4.85E-01	2.05E-01	2.16E-02	1.29E-04	Furnace (heating): 0.90 kWh
Ozone depletion	kg CFC-11 eq	1.36E-08	5.76E-09	6.06E-10	3.64E-12	Furnace (reaction): 0.38
Human toxicity	kg 1,4-DB eq	9.32E-02	3.93E-02	4.14E-03	2.48E-05	Mechanical Syringe Pump: 0.04kWh
Photochemical oxidant forma	kg NMVOC	1.12E-03	4.72E-04	4.97E-05	2.98E-07	Mass flow controller:
Particulate matter formation	kg PM10 eq	4.50E-04	1.90E-04	2.00E-05	1.20E-07	0.00024 kWh (per unit
Ionising radiation	kg U235 eq	2.16E-01	9.11E-02	9.59E-03	5.75E-05	per hour)
Terrestrial acidification	kg SO2 eq	1.45E-03	6.12E-04	6.44E-05	3.86E-07	
Freshwater eutrophication	kg P eq	1.29E-04	5.46E-05	5.74E-06	3.45E-08	
Marine eutrophication	kg N eq	3.58E-04	1.51E-04	1.59E-05	9.55E-08	Electricity impacts based
Terrestrial ecotoxicity	kg 1,4-DB eq	8.04E-06	3.40E-06	3.57E-07	2.14E-09	on 2009 UK Grid Mix, as
Freshwater ecotoxicity	kg 1,4-DB eq	1.97E-03	8.32E-04	8.76E-05	5.26E-07	stated in the Department
Marine ecotoxicity	kg 1,4-DB eq	2.15E-03	9.08E-04	9.55E-05	5.73E-07	of Energy & Climate
Agricultural land occupation	m2a	6.04E-03	2.55E-03	2.69E-04	1.61E-06	Change (DECC), Digest
Urban land occupation	m2a	1.97E-03	8.34E-04	8.77E-05	5.26E-07	of United Kingdom
Natural land transformation	m2	1.10E-04	4.66E-05	4.90E-06	2.94E-08	Energy Statistics
Water depletion	m3	2.77E-03	1.17E-03	1.23E-04	7.39E-07	(DUKES), available from
Metal depletion	kg Fe eq	2.99E-03	1.26E-03	1.33E-04	7.99E-07	www.decc.gov.uk
Fossil depletion	kg oil eq	1.58E-01	6.66E-02	7.01E-03	4.21E-05	

Infrastructure Impacts

Impact category	Unit	Furnace	Mechanical Syringe	Mass Flow Controller(s)	Notes:
Climate change	kg CO2 eq	1.43E+02	1.17E+01	9.60E+00	Impacts quoted in this table are for the complete assembled infrastucture equipment.
Ozone depletion	kg CFC-11 eq	1.22E-05	1.06E-06	8.71E-07	The impacts quoted for the per batch
Human toxicity	kg 1,4-DB eq	1.79E+02	4.54E+01	3.53E+01	synthesis of MWNT is based off
Photochemical oxidant forma	kg NMVOC	4.82E-01	4.49E-02	3.37E-02	operating and lifetime assumptions of the
Particulate matter formation	kg PM10 eq	3.89E-01	2.45E-02	1.98E-02	various pieces of laboratory equipment.
Ionising radiation	kg U235 eq	5.06E+01	4.83E+00	3.50E+00	
Terrestrial acidification	kg SO2 eq	9.75E-01	6.00E-02	5.65E-02	→ Impacts that arise, per batch, of
Freshwater eutrophication	kg P eq	1.37E-01	3.02E-02	2.31E-02	MWNTs grown (as % of values stated in
Marine eutrophication	kg N eq	1.47E-01	1.49E-02	1.22E-02	this table):
Terrestrial ecotoxicity	kg 1,4-DB eq	3.34E-02	1.77E-03	2.00E-03	
Freshwater ecotoxicity	kg 1,4-DB eq	3.25E+00	6.22E-01	4.51E-01	Furnace: 0.00667 %
Marine ecotoxicity	kg 1,4-DB eq	3.49E+00	6.05E-01	4.50E-01	Mechanical Syringe: 0.02 %
Agricultural land occupation	m2a	4.72E+00	2.56E-01	1.45E-01	Mass Flow Controller:
Urban land occupation	m2a	1.71E+00	2.68E-01	2.02E-01	0.02 % per unit → 0.04% overall
Natural land transformation	m2	3.57E-02	1.75E-03	1.21E-03	
Water depletion	m3	1.42E+00	1.25E-01	1.32E-01	
Metal depletion	kg Fe eq	1.28E+02	1.32E+01	6.92E+00	
Fossil depletion	kg oil eq	4.62E+01	3.71E+00	2.59E+00	

Appendix C.3 Inventory Data – used in the LCA of MWCNT synthesis via CVD

Appendix C.3.1. Chemical Materials Used

	Quantity	Representative Dataset
Ferrocene	0.2 g	See Table below
Toluene	8.67 g (i.e. 10ml)	Toluene, liquid, at plant/RER U
Argon	Heating: 14.71 g Reaction: 44.1 g Cooling: 14.71 g	Argon, liquid, at plant/RER U
Hydrogen	0.247 g	
Hydrochloric acid	23.68 g	Hydrochloric acid, from Mannheim process, at plant/RER U

Name	Amount	Unit	Quantity	Allocation	Category	Comment
Ferrocene (latest aspen) adjusted Nitrogen	170	g	Mass	100 %	Chemicals\Inorganic	91.5% yield

Known inputs from technosphere (materials/fuels)

Name	Amount	Unit	Comment
Iron (III) chloride, 40% in H2O, at plant/CH U	86.193	g	
Iron scrap, at plant/RER U	43.08	g	
Water, deionised, at plant/CH U	1130	g	
Sodium methoxide, at plant/GLO U	121.5	g	
Benzene, at plant/RER U	132	g	Verified through Finechem as the closest available, suitbaly similar, chemical representation of cyclopentadiene.
Methanol, at plant/GLO U	471.96	g	
Sulphuric acid, liquid, at plant/RER U	3210	g	
Nitrogen, liquid, at plant/RER U	0.259	g	
(Insert line here)			

Known inputs from technosphere (electricity/heat)

Name	Amount	Unit	Comment
Electricity, production mix GB/GB U - DUKES2009	0.481	kWh	Mixing energy
Heat, unspecific, in chemical plant/RER U	0.021	kWh	Heat requirement

Known outputs to technosphere. Waste and emissions to treatment

Name	Amount	Unit	Comment
Waste water - untreated, organic contaminated EU-27 S	4.61	kg	

Appendix C.3.2. Mass flow controller (MFC)

Data source origin: Series FMA-700A Mass Flow Controller, data sheet. Empirical measurements and judgements.

Component	Material	Quantity	Representative Dataset
Outer Casing	**Glass Reinforced Nylon**	**96 g**	**Glass fibre reinforced plastic, polyamide, injection moulding, at plant/RER U**
Gas fittings fasteners and bolts	**Stainless steel**	**380 g**	**Stainless steel hot rolled coil, annealed & pickled, elec. arc furnace route, prod. mix, grade 304 RER S**
Gas orifice block	**Aluminium**	**70 g**	**Aluminium, production mix, cast alloy, at plant/RER U**
Panel display		**19 g**	**Flat glass, uncoated, at plant/RER S**
Washers	**Brass**	**30 g**	**Brass, at plant/CH U**
Seals	**Synthetic Rubber**	**20 g**	**Synthetic rubber, at plant/RER U**
O-rings	**FKM**	**10 g**	**Polyvinylfluoride, at plant/US S**
Electronic Components	**Capacitor, connectors, inductors, resistors etc.**	**20 g**	**Electronic component, unspecified, at plant/GLO U**
Printed wiring board	**Copper, glass fibre, etc.**	**0.005 m^2**	**Printed wiring board, surface mount, lead-containing surface, at plant/GLO U**

Appendix C.3.3. MECHANICAL SYRINGE PUMP

Component	Material	Quantity	Representative Dataset
Main structure	**Steel**	**1,000 g**	**Steel, low-alloyed, at plant/RER U**
Electric motor	**Majority, steel & copper**	**12 g**	**Copper, from combined metal production, at refinery/SE U**
Outer casing	**Polypropylene**	**200 g**	**Polypropylene resin, at plant/RNA**
Syringe	**Glass**	**100 g**	**Packaging glass, white, at regional storage/CH S**
Printer Wiring Board	**Copper, glass fibre, etc**	**0.0005 m^2**	**Printed wiring board, surface mount, lead-containing surface, at plant/GLO U**
Power light indicators	**L.E.D.**	**2 g**	**Light emitting diode, LED, at plant/GLO U**
Electronic components	**Capacitor, connectors, inductors, resistors etc**	**10 g**	**Electronic component, active, unspecified, at plant/GLO U**
Power supply unit		**5% of a unit used for a laptop computer**	**Power supply unit, at plant/CN U**
Tubing	**Synthetic rubber**	**100 g**	**Synthetic rubber, at plant/RER U**

Appendix C.3.4. HORIZONTAL GAS FLOW FURNACE

Component	Material	Quantity	Representative Dataset
Main structure	**Steel**	**14, 000 g**	**Steel, low-alloyed, at plant/RER U**
Heating element	**Nickel**	**1, 280 g**	**Nickel, secondary, from electronic and electric scrap recycling, at refinery/SE U**
Ceramic tubing	**Silicon carbide**	**3, 800 g**	**Silicon carbide, at plant/RER U**
Outer thermal shield	**Aluminium**	**1, 000 g**	**Aluminium, production mix, cast alloy, at plant/RER U**
Insulation	**Rockwool**	**0.03 x 2.00 m**	**Insulation spiral-seam duct, rockwool, DN 400, 30 mm, at plant/RER U**
Internal cabling	**Cable, connectors and plugs etc.**	**3 m**	**Cable, connector for computer, without plugs, at plant/GLO U**
Reaction tube	**Glass tube, borosilicate**	**2, 000 g**	**Glass tube, borosilicate, at plant/DE U**
Power supply unit			

Quantity	Representative Dataset
2 of	**Ecoinvent: Plugs, inlet and outlet, for computer cable, at plant/GLO U**
50 g	**Ecoinvent: Switch, toggle type, at plant/GLO U**
500 g	**Ecoinvent: Printed wiring board, power supply unit desktop PC, solder mix, at plant/GLO U**

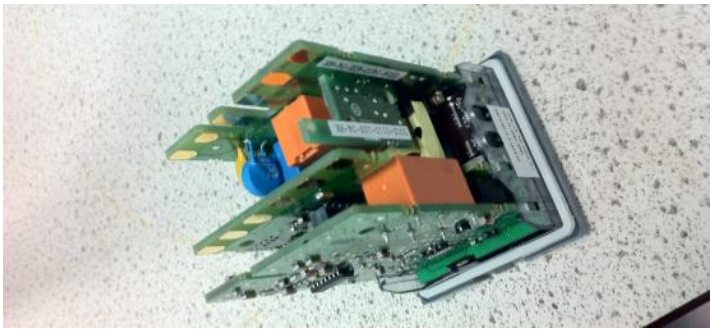
Component	Material	Quantity	Representative Dataset
Furnace Controller			

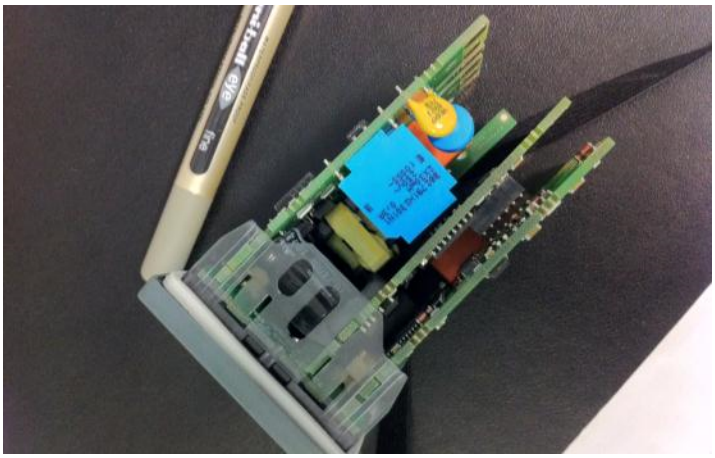
Materials/Assemblies	Amount	Unit	Comment
Capacitor, electrolyte type, < 2cm height, at plant/GLO U	2.99	g	
Capacitor, SMD type, surface-mounting, at plant/GLO U	1.665	g	
Connector, clamp connection, at plant/GLO U	3	g	
Diode, glass-, SMD type, surface mounting, at plant/GLO U	0.5	g	
Inductor, ring core choke type, at plant/GLO U	3	g	
Inductor, ring core choke type, at plant/GLO U	3	g	used to model relay
Integrated circuit, IC, logic type, at plant/GLO U	1.7	g	
Light emitting diode, LED, at plant/GLO U	6.8	g	
Resistor, metal film type, through-hole mounting, at plant/GLO U	0.2	g	
Resistor, metal film type, through-hole mounting, at plant/GLO U	1	g	used to model thermistor
Resistor, SMD type, surface mounting, at plant/GLO U	0.765	g	
Transformer, low voltage use, at plant/GLO U	33.6	g	
Printed wiring board, surface mount, lead-containing surface, at plant/GLO U	0.036/2 = 0.018	m2	
Printed wiring board, through-hole, lead-containing surface, at plant/GLO U	0.036/2 = 0.018	m2	
High density polyethylene resin, at plant/RNA	150	g	
Steel, converter, low-alloyed, at plant/RER U	150	g	
Synthetic rubber, at plant/RER U	3	g	buttons and gaskets
Cable, ribbon cable, 20-pin, with plugs, at plant/GLO U	200	g	
Solder, bar, Sn95.5Ag3.9Cu0.6, for electronics industry, at plant/GLO U	3	g	

Solid State Relay

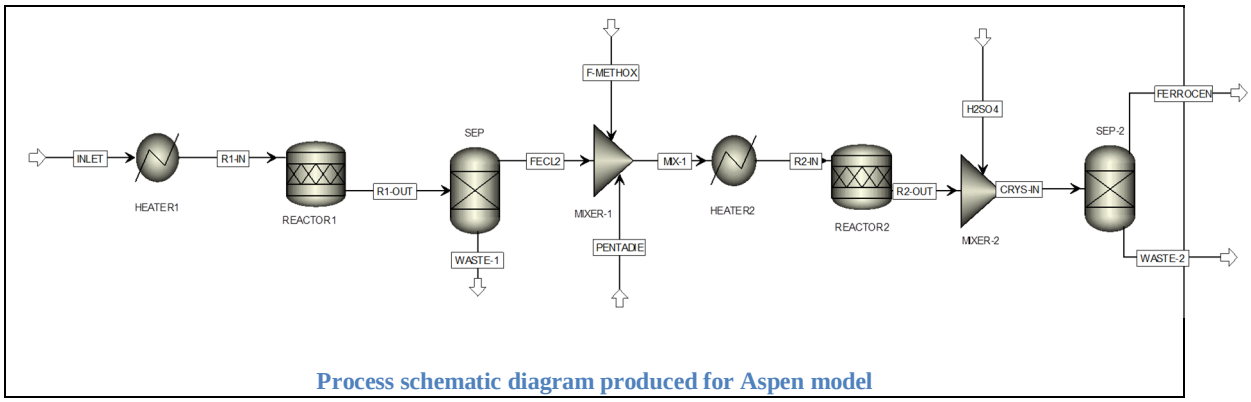
Materials/Assemblies	Amount	Unit	Comment
Diode, glass-, through-hole mounting, at plant/GLO U	2	g	
Light emitting diode, LED, at plant/GLO U	0.2	g	
Electronic component, unspecified, at plant/GLO U	5	g	To cover other internal electrical components
Copper, from imported concentrates, at refinery/DE U	100	g	bus bar
Polycarbonate, at plant/RER U	100	g	casing
Steel, low-alloyed, at plant/RER U	100	g	mounting / casing

Appendix C.3.5. PHOTOGRAPHS OF MAIN FURNACE CONTROLLER





APPENDIX D: SUPPLEMENTARY INFORMATION: FERROCENE INVENTORY DATA.



Process schematic diagram produced for Aspen model

Process Information Sources:

- US Patent Office 3,217,022 patented November 9,1965, *Production of ferrocene compounds* (Cordes 1965).
- PubChem substance database (National Center for Biotechnology Information 2011a)

Patent route 4 (Cordes 1965) outlines a process for the continuous production of ferrocene rather than batch productions, with a reported yield of 85-98%. Since a continuous process is the most likely to be adopted for an industrial level production route this was adopted as our 'model' process.

Through the use of the industrial chemical substance database PubChem (National Center for Biotechnology Information 2011a) significant confidence in at least the input materials could be established, since three synthetic routes of ferrocene production are presented, electrochemical reduction, metal oxide and cyclopentadiene sodium + ferrous chloride route. The proportion of ferrocene produced via these discrete pathways are not readily available in the literature, it was therefore assumed, in-line with the references found and other academic sources (Oxford 1996) that the latter pathway stated in PubChem and in conjunction with the found patent would be the most suitable process to model.

All temperatures, pressures, relative quantities of input materials and residence times of the separate process steps are in alignment to the information provided in the patent.

Chemical Reaction

Reactor 1 –Production of ferrous chloride, $FeCl_2$, from ferric chloride, $FeCl_3$.

$$⅔FeCl_3 + ⅓Fe \rightarrow \frac{65°C}{1\ bar}, \text{ 95\% efficiency} \rightarrow FeCl_2$$

Overall Process

$$FeCl_2 + 2CH_3ONa + 2C_5H_5 \rightarrow Fe\ (C_5H_5)_2 + 2NaCl + 2CH_3OH$$

Appendix D.1 ASSUMPTIONS

Temperature and Pressure, of 20°C (293.15 K) and 1 atm (101.325 kPa)

1. ***Process efficiency:*** 91.5% yield (i.e. midway between 85-98% yield stated in patent)

2. ***Reaction conditions:*** All processes occur at ambient pressure, only reactor 1 is heated, and this to 65°C, Aspen model revealed that addition of downstream chemicals would decrease fluid temperature to approximately 40°C, this is deemed sufficient for subsequent chemical reactions to take place – considered a realistic scenario since industrial plants are unlikely to input additional unnecessary heat.

3. ***Heating Energy requirement:*** calculated using Aspenfor the heat duty of reactor 1 to be 0.021kWh

4. ***Nitrogen:*** To prevent the oxidation of iron species the process reactions occur under a protective atmosphere of nitrogen. Using a rule of thumb principle adopted by many laboratory chemists, a 5 % of nitrogen is used relative to the flow rate of the materials in the reaction vessel, calculated using the density of nitrogen at normal temperature and pressure.

5. ***Mixing energy:*** Viscosity of water used as a representative of the mixed substances. This assumption is deemed valid since conducting checks of the viscosity of fluid through the processes, e.g. R2-IN at a temperature of 313K

calculated to be 4.8 x 10^{-4} N.s.m^{-2}, with water at 298 K being 8.9 x 10^{-4} N.s.m^{-2}, i.e. values within the same order of magnitude unlikely to require significantly different rotational energy requirement.

Mixer 1, flow rate =2.68ml/min

Residence time of each vessel assumed 90 minutes, as per patent.

Using residence time, T = $\frac{volume}{flow\ rate}$

➔ Volume = 241ml

This volume represents 0.0201% of maximum volume of a found laboratory stirring vessel. Stirring vessel has a maximum fluid mixing capacity of 12,000ml and maximum power requirement of 0.75kW

➔ 0.75 kW * 0.0201% = 0.0151kW

Mixer 2, flow rate =82.9ml/min

- Similarly to above, volume = 7,463ml
- 0.466kW

Total, $\sum mixer\ energies$ = 0.481kW

Verified this assumption with a 5litre vessel stirred with a laboratory magnetic stirrer, at full rate, 0.009 kW of power being drawn = 0.54kWh

One hour of operation

∴ 0.481kWh

Residence time: used for the heating and stirring periods, were tjose

Separators, *(SEP and SEP -2):* Perfect separation of waste from desired products have been assumed, this could be determined as an unrealistic scenario, however without specific process information this is a sensible and transparent first estimate.

Appendix D.2 CHEMICAL SOURCE:

Input Chemicals	Quantity [g]	Inventory Data Source
Iron (III) Chloride	**86.193**	**Ecoinvent**
Iron scrap	**43.08**	**Ecoinvent**
Water, deionised	**1130**	**Ecoinvent**
Sodium methoxide	**121.5**	**Ecoinvent**
Benzene (in place of cyclopentadienide)	**132**	**Finechem – benzene found closest match using a range of similar ringed carbon compounds available in inventory data sources. Therefore substituted (based on molar amounts) cyclopentadienide with benzene dataset in Ecoinvent.**
Methanol	**471.96**	**Ecoinvent**
Sulphuric acid	**3210**	**Ecoinvent**
Nitrogen	**0.259**	**Ecoinvent**

Appendix D.2.1. WASTE WATER

Waste Chemicals	**4610 [g]**	**Modelled as Ecoinvent process 'Waste water - untreated, organic contaminated EU-27 S'**

Appendix D.2.2. HEAT DATASET

0.021kWh of heat, modelled using Ecoinvent dataset 'Heat, unspecific, in chemical plant/RER U'

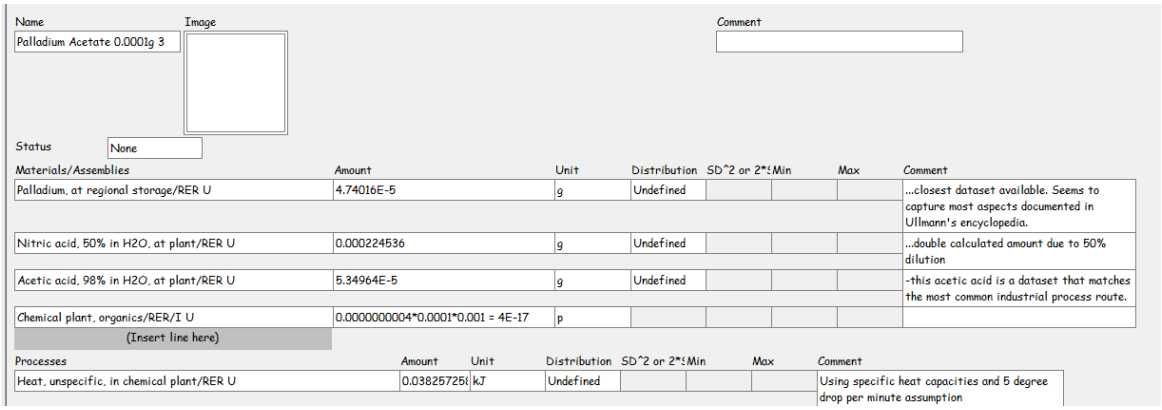
Title:	Analysing 1 kg 'Ferrocene (latest aspen)'																				
Method:	ReCiPe Midpoint (H) V1.05 / Europe ReCiPe H								Cumulative Energy Demand V1.08 / Cumulative energy demand												
Indicator:	Characterisation																				
Impact category	Unit	Total	Fossil depletion	Metal depletion	Water depletion	Natural land transformation	Urban land occupation	Agricultural land occupation	Marine ecotoxicity	Freshwater ecotoxicity	Terrestrial ecotoxicity	Marine eutrophication	Freshwater eutrophication	Terrestrial acidification	Ionising radiation	Photochemical oxidant formation	Human toxicity	Ozone depletion	Climate change	Cumulative Energy Demand	
Climate change	kg CO2 eq	**1.2E+01**	4.1E-01	1.1E-02	5.3E-03	3.5E+00	1.4E+00	2.1E+00	2.3E+00	4.8E-02	3.0E-04	2.3E+00	4.2E-02	1.0E-03	1.5E-02	4.8E-03	1.2E-02	1.3E-02	1.0E+00	2.3E-02	1.0E+00
Ozone depletion	kg CFC-11 eq	**1.5E-06**	5.3E-07	1.2E-09	2.5E-09	2.7E-07	2.4E-10	4.5E-07	2.4E-07	3.2E-09	1.5E-08	2.4E-07	2.1E-09	1.6E-08	1.9E-08	1.7E-08	1.9E-08	1.0E-08	1.0E-08	1.3E-08	1.0E-08
Human toxicity	kg 1,4-DB eq	**4.9E+00**	5.6E-01	9.0E-03	4.9E-03	2.1E+00	1.2E-02	2.1E-01	1.9E+00	2.8E-02	5.6E-02	1.9E+00	2.8E-02	1.2E-02	1.2E-02	1.2E-02	1.2E-02	1.2E-02	1.2E-02	1.1E-02	1.2E-02
Photochemical oxidant formation	kg NMVOC	**6.0E-02**	1.1E-03	8.6E-05	1.4E-05	8.3E-03	4.4E-03	4.3E-03	3.6E-02	8.5E-05	7.2E-04	1.0E-04	1.8E-04	9.6E-04	1.4E-03	1.4E-03	1.4E-03	1.4E-03	1.4E-03	4.8E-03	1.4E-03
Particulate matter formation	kg PM10 eq	**6.4E-02**	6.8E-04	3.0E-05	8.2E-06	5.5E-03	1.4E-03	1.1E-03	5.3E-02	5.5E-05	3.0E-04	4.7E-05	4.2E-05	8.5E-05	1.4E-04	1.4E-04	1.4E-04	1.4E-04	1.4E-04	1.5E-03	1.4E-04
Ionising radiation	kg U235 eq	**3.2E+00**	2.7E-01	2.8E-03	5.1E-03	2.1E+00	4.2E-04	1.4E-01	5.6E-01	3.4E-02	1.4E-01	4.1E-01	1.4E-02	2.4E-04	3.0E-05	6.9E-03	6.9E-03	6.9E-03	6.9E-03	6.9E-03	6.9E-03
Terrestrial acidification	kg SO2 eq	**2.8E-01**	1.9E-03	6.7E-05	2.2E-05	1.6E-02	4.5E-03	3.2E-03	2.5E-01	1.8E-04	9.6E-04	1.5E-04	5.8E-06	3.0E-05	2.5E-03	4.7E-03	4.7E-03	4.7E-03	4.7E-03	4.7E-03	4.7E-03
Freshwater eutrophication	kg P eq	**4.9E-03**	4.3E-04	6.4E-06	4.4E-06	2.7E-03	1.1E-05	2.5E-04	1.4E-03	4.2E-05	8.5E-05	5.8E-06	1.6E-06	2.5E-03	1.6E-06	1.6E-06	1.6E-06	1.6E-06	1.6E-06	1.6E-06	1.6E-06
Marine eutrophication	kg N eq	**1.4E-02**	4.3E-04	2.9E-05	5.3E-06	3.0E-03	8.5E-04	1.0E-03	6.0E-03	3.6E-05	2.4E-04	3.0E-05	2.5E-03	3.0E-05	3.0E-05	3.0E-05	3.0E-05	3.0E-05	3.0E-05	3.0E-05	3.0E-05
Terrestrial ecotoxicity	kg 1,4-DB eq	**9.6E-04**	8.0E-05	1.5E-06	1.5E-06	3.0E-04	2.6E-05	1.9E-04	3.4E-04	3.2E-06	5.3E-06	7.2E-06	1.3E-05	1.3E-05	1.3E-05	1.3E-05	1.3E-05	1.3E-05	1.3E-05	1.3E-05	1.3E-05
Freshwater ecotoxicity	kg 1,4-DB eq	**9.0E-02**	7.6E-03	1.3E-04	8.8E-05	4.1E-02	4.0E-04	6.7E-03	3.2E-02	5.9E-04	1.3E-03	1.0E-04	2.0E-05	2.0E-05	2.0E-05	2.0E-05	2.0E-05	2.0E-05	2.0E-05	2.0E-05	2.0E-05
Marine ecotoxicity	kg 1,4-DB eq	**9.1E-02**	8.0E-03	1.4E-04	8.3E-05	4.1E-02	6.7E-04	4.6E-03	3.4E-02	5.9E-04	1.4E-03	1.5E-04	1.0E-04	1.0E-04	1.0E-04	1.0E-04	1.0E-04	1.0E-04	1.0E-04	1.0E-04	1.0E-04
Agricultural land occupation	m2a	**2.4E-01**	2.5E-02	1.2E-03	2.4E-04	6.0E-02	2.5E-05	3.3E-03	1.5E-01	5.5E-04	4.0E-03	3.2E-04	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00
Urban land occupation	m2a	**6.1E-02**	4.6E-03	6.1E-04	1.3E-04	1.8E-02	5.2E-05	4.1E-03	3.2E-02	1.4E-04	1.3E-03	1.1E-04	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00
Natural land transformation	m2	**2.8E-03**	6.9E-05	7.1E-06	1.3E-06	6.1E-04	-3.7E-09	1.1E-03	9.4E-04	4.6E-06	7.3E-05	1.7E-05	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00
Water depletion	m3	**9.8E-01**	6.2E-03	5.9E-05	8.4E-03	3.9E-02	9.1E-04	5.1E-03	9.4E-01	3.5E-04	1.8E-03	6.4E-05	-1.8E-02	-1.8E-02	-1.8E-02	-1.8E-02	-1.8E-02	-1.8E-02	-1.8E-02	-1.8E-02	-1.8E-02
Metal depletion	kg Fe eq	**1.0E+00**	9.8E-02	2.6E-03	4.9E-04	1.7E-01	8.0E-04	4.2E-02	7.0E-01	5.5E-04	2.0E-03	2.8E-04	3.2E-04	3.2E-04	3.2E-04	3.2E-04	3.2E-04	3.2E-04	3.2E-04	3.2E-04	3.2E-04
Fossil depletion	kg oil eq	**6.1E+00**	1.2E-01	3.5E-03	1.5E-03	1.3E+00	1.2E+00	2.4E+00	7.7E-01	1.2E-02	1.0E-01	2.4E-02	1.5E-01	1.5E-01	1.5E-01	1.5E-01	1.5E-01	1.5E-01	1.5E-01	1.5E-01	1.5E-01
Cumulative Energy Demand	MJ	**3.0E+02**	8.3E+00	1.9E-01	1.3E-01	7.9E+01	5.3E+01	1.0E+02	4.0E+01	9.1E-01	6.0E+00	1.1E+00	6.7E+00	6.7E+00	6.7E+00	6.7E+00	6.7E+00	6.7E+00	6.7E+00	6.7E+00	6.7E+00

APPENDIX E: SUPPORTING DATA FOR CHAPTER 5; FE-PD-SiO_2

Appendix E.1 CHEMICAL DATASET MODELLING

Taken from paper: The allocation of total impacts to the desired products is deemed a justifiable assumption, since the co-production of NO is of lesser economic value than the metal compounds formed. However, if allocation on a mass basis were to occur then $Fe(NO_3).9H_2O$ and $Pd(OAc)_2$ would have 89% and 71.5% of the impacts reported in this study respectively.

Appendix E.1.1. PALLADIUM ACETATE CREATED DATASET

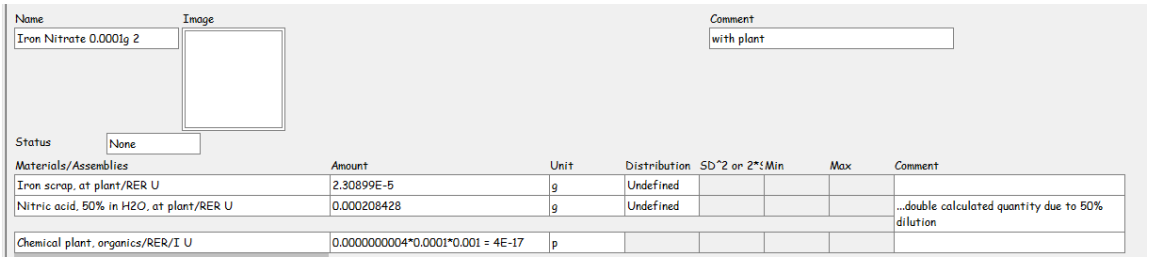


Name: Palladium Acetate 0.0001g 3 | Image | Comment | Status: None

Materials/Assemblies	Amount	Unit	Distribution	SD^2 or 2*Min	Max	Comment
Palladium, at regional storage/RER U	4.74016E-5	g	Undefined			...closest dataset available. Seems to capture most aspects documented in Ullmann's encyclopedia.
Nitric acid, 50% in H2O, at plant/RER U	0.000224536	g	Undefined			...double calculated amount due to 50% dilution
Acetic acid, 98% in H2O, at plant/RER U	5.34964E-5	g	Undefined			-this acetic acid is a dataset that matches the most common industrial process route.
Chemical plant, organics/RER/I U	0.0000000004*0.0001*0.001 = 4E-17	p				
(Insert line here)						

Processes	Amount	Unit	Distribution	SD^2 or 2*Min	Max	Comment
Heat, unspecific, in chemical plant/RER U	0.03825725(	kJ	Undefined			Using specific heat capacities and 5 degree drop per minute assumption

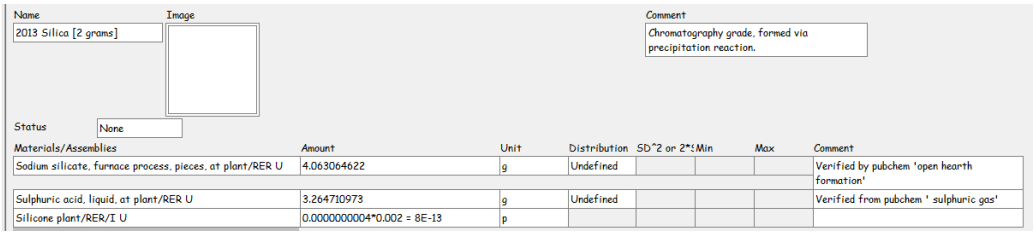
Appendix E.1.2. IRON NITRATE CREATED DATASET



Name: Iron Nitrate 0.0001g 2 | Image | Comment: with plant | Status: None

Materials/Assemblies	Amount	Unit	Distribution	SD^2 or 2*Min	Max	Comment
Iron scrap, at plant/RER U	2.30899E-5	g	Undefined			
Nitric acid, 50% in H2O, at plant/RER U	0.000208428	g	Undefined			...double calculated quantity due to 50% dilution
Chemical plant, organics/RER/I U	0.0000000004*0.0001*0.001 = 4E-17	p				

Appendix E.1.3. CHROMATOGRAPHY GRADE SILICA CREATED DATASET



Name: 2013 Silica [2 grams] | Image | Comment: Chromatography grade, formed via precipitation reaction. | Status: None

Materials/Assemblies	Amount	Unit	Distribution	SD^2 or 2*Min	Max	Comment
Sodium silicate, furnace process, pieces, at plant/RER U	4.063064622	g	Undefined			Verified by pubchem 'open hearth formation'
Sulphuric acid, liquid, at plant/RER U	3.264710973	g	Undefined			Verified from pubchem ' sulphuric gas'
Silicone plant/RER/I U	0.0000000004*0.002 = 8E-13	p				

Appendix E.2 SYNTHESIS PATHWAY MODELLED

Name: Cat_Fe_Synthesis | Image | Comment: Cradle-to-gate impacts 1 gram of Cat_Fe

Status: None

Materials/Assemblies	Amount	Unit	Distribution	SD^2 or 2*S	Min	Max
a 20wt%Fe/SiO2	1/2.72 = 0.368	p				
Methanol	0.368	p	Undefined			
Silica [2 grams]	0.368	p	Undefined			
Water Usage	0.368	p	Undefined			
Hydrogen gas used - pretreat	0.368	p	Undefined			
1. Mechanical Stirrer Elec (incl 4)	0.368	p	Undefined			
2. Mechanical Stirrer Elec	0.368	p	Undefined			
3. Mechanical Stirrer Elec	0.368	p	Undefined			
5. Sonicator Elec	0.368	p	Undefined			
6i. Rotional Evaporator	0.368	p	Undefined			
6ii. Rotational Evaporator - Water Bath	0.368	p	Undefined			
6iii. Rotational Evaporator - Pump	0.368	p	Undefined			
7. Furnace	0.368	p	Undefined			
8. H. Furnace - Ramp-up	0.368	p	Undefined			
9. H. Furnace - Pre-treatment	0.368	p	Undefined			
10. H. Furnace - 2nd ramp-up	0.368	p	Undefined			
Mechanical stirrer	0.368*1.3699E-04 = 5.04E-5	p				
Sonicator_2013	0.368*1.3699E-04 = 5.04E-5	p				
Rotary Evaporator & Bath_2013	0.368*9.1324E-05 = 3.36E-5	p				
Vacuum Pump	0.368*1.3699E-04 = 5.04E-5	p				
Furnace 1100C_2013	0.368*2.2831E-05 = 8.4E-6	p				
Horizontal Reactor_2013	0.368*5.4795E-05 = 2.02E-5	p				
MFC Infrastructure_revised_2013	0.368*9.1324E-05 = 3.36E-5	p				
(Insert line here)						

Appendix E.3 RELATIVE SURFACE AREAS OF CATALYSTS

Brunauer–Emmett–Teller (BET) (Brunauer *et al.* 1938) measurements recorded for Fe-Pd-SiO2 catalysts. More detail contained with PhD thesis of Dr Rhodri Owen (Unversity of Bath, 2014), data kindly supplied from this source.

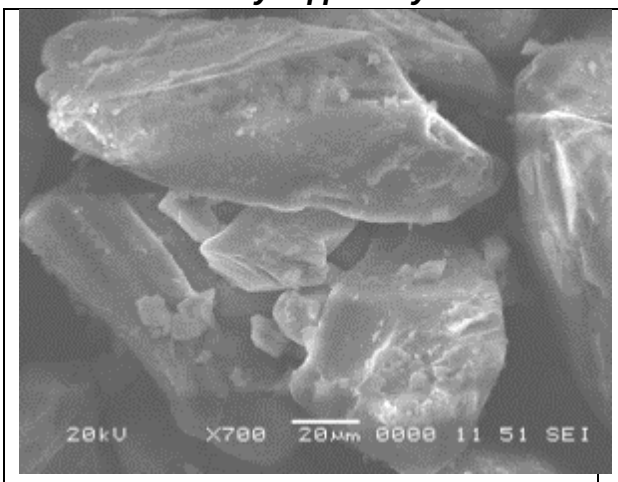
Catalyst	**10wt%Fe/1wt%Pd /SiO_2**	**20wt%Fe/1wt%Pd /SiO_2**	**30wt%Fe/1wt%Pd /SiO_2**	**40wt%Fe/1wt%Pd /SiO_2**
Surface Area (m^2g^{-1})	**378.8**	**281.1**	**269.5**	**249.1**

Catalyst	**20wt%Fe/1wt%Pd /SiO_2**	**20wt%Fe/2wt%Pd /SiO_2**	**20wt%Fe/3wt%Pd /SiO_2**	**20wt%Fe/4wt%Pd /SiO_2**
Surface Area (m^2g^{-1})	**281.1**	**311.3**	**325.2**	**330.7**

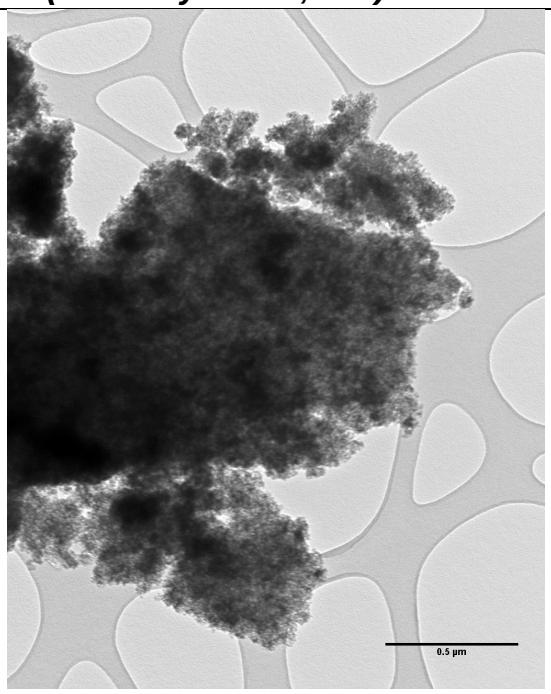
Appendix E.4 Electron Microscopy Images

- SEM recorded on a JEOL 6480LV at 5-20 kV.
- TEM recorded using a JEOL 1200 operated at 120 kV.
- Samples were prepared in ethanol and deposited onto copper or nickel grids.

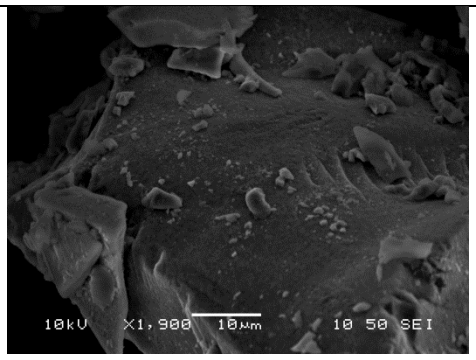
Kindly supplied by Dr Rhodri Owen (University of Bath, 2014).

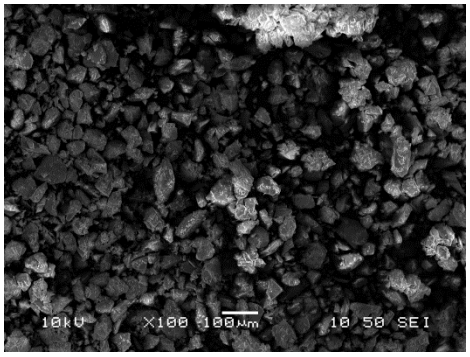


SEM Image Recorded for 20wt%Fe/SiO_2

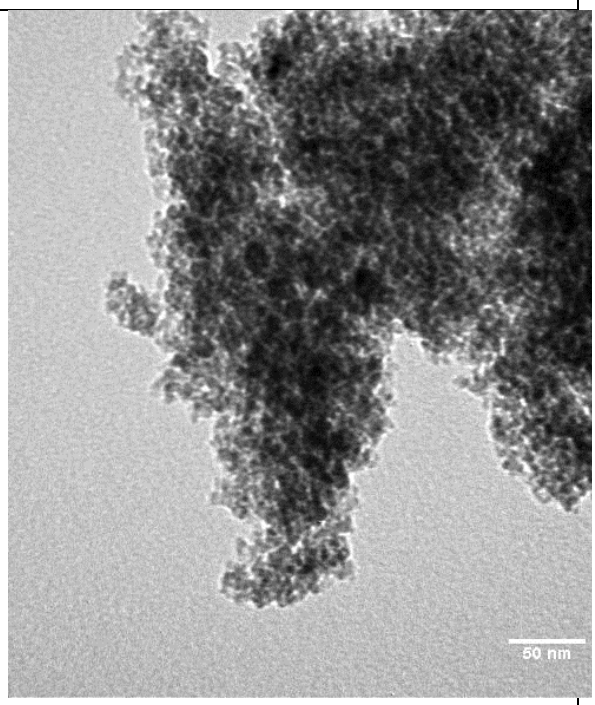


TEM Image Recorded for 20wt%Fe/SiO_2





SEM Images Recorded for



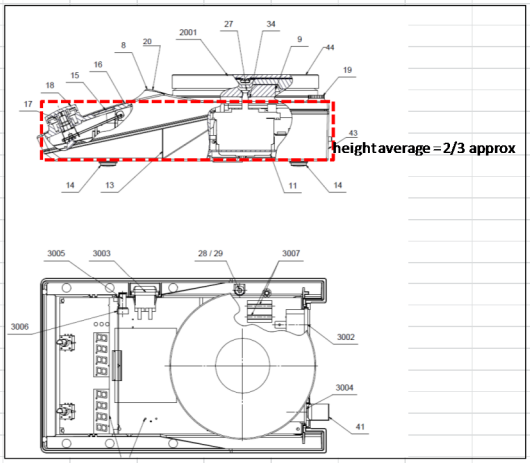
TEM Image Recorded for

20wt%Fe/1wt%Pd/SiO_2	20wt%Fe/1wt%Pd/SiO_2

Appendix E.5 ADDITIONAL INFRASTRUCTURE

Appendix E.5.1. MECHANICAL STIRRER

	Manufacturer (Model)		
	IKA (38100)		
Dimensions			
Dimensions (W x H x D)	160 x 85 x 270	mm	
Weight	2.5	kg	
Surface area of panels	0.9722	m2	
Volume	0.002	m3	
Density	1031.6	kg/m3	
EC-Motor 24V			
Hot plate	130mmdia		
	18mm height		
Electronic control unit			
Metal approx 1.5mm thickness			
Plastic coating approx 1mm			
Approx material breakdown:			
	%	Mass	
Screws, fasteners etc.	5%	0.125	
Hot plate	10%	0.25	
Plastic coverings, controls etc	10%	0.25	
Electrical components, thermocouples, IC, wiring etc.	10%	0.25	
Electric Motor	20%	0.5	
Steel housing	45%	1.125	



Name	Image	Comment
Mechanical stirrer		Assumptions. Based on manufacturer supplied drawing. And likely material compositions

Status: None

Materials/Assemblies	Amount	Unit	Distribution	SD^2 or 2*SMin		Max	Comment
Steel, low-alloyed, at plant/RER U	1	kg	Undefined				mostly steel construction casing material, fasteners etc.
CD-ROM/DVD-ROM drive, desktop computer, at plant/GLO U	1	p	Undefined				Mass of component = 0.9kg chosen this dataset since the motor, controller, casing complexity, operating voltage of 12v for most cd driveds however some run at 24V relate to 24v of stirrer motor. Torque similar. Missing- variable speed controller
Electronics for control units/RER U	0.05	kg	Undefined				Think much of electronic will be covered above, additional electronics added to account for heating operation.
Nickel, 99.5%, at plant/GLO U	0.20	kg	Undefined				heating element
Polypropylene injection moulding E	0.25	kg	Undefined				common plastic used in appliances, likely candidate
Aluminium, production mix, at plant/RER U	0.10	kg	Undefined				

Appendix E.5.2. ROTARY EVAPORATOR AND BATH

Rotary Evaporator & Bath					
http://www.highervacuum.com/product/p7/Divac0.6L_1.2L_2.2L.pdf					
Overall weight	16-18kg, dependent on glass assembly				
Table 3-4: Materials used	Component / Material designation				
		Stainless Steel	PBT	Al	
	15.85				
Housing Rotavapor Aluminium	7			7	
Guides lift Hardened steel / stainless steel	2.5	2.5			
Casting components PBT partially glass reinforced	2		2		
Housing bath PBT partially glass reinforced	1		1		
Bath Stainless steel	1	1			
Protective ring PBT partially glass reinforced	0.25		0.25		
~~Protective shield Polycarbonate~~	Not used				
Center rotation drive Stainless steel	0.5	0.5			
Condenser flange Aluminium	0.5			0.5	
Seal NBR, Teflon	0.1				
Electronic components	1	*covering control units, displays etc.			
Copper windings	0.15	*brushless DC motor for spinning, DC motor for lifting. Approx material estimates			
Glassware: tubing, flasks etc.	1	*separate to rest of housing weight			

Electric Motor
http://in.rsdelivers.com/catalogue/category/ac-geared-motors/206.aspx#A-165256|A-37854|PI-1|PS-25|

Supplementary info from another manufacturer:
http://www.yamato-usa.com/products/evaporators/re300600800.htm

3.2 Materials used

Table 3-4: Materials used

Component	Material designation
Housing Rotavapor	Aluminium
Guides lift	Hardened steel / stainless steel
Casting components	PBT partially glass reinforced
Housing bath	PBT partially glass reinforced
Bath	Stainless steel
Protective ring	PBT partially glass reinforced
Protective shield	Polycarbonate
Center rotation drive	Stainless steel
Condenser flange	Aluminium
Seal	NBR, Teflon

Name: Rotary Evaporator & Bath_20 | Image | Comment: Data based on manufacturer brochure. **new/amended datasets 07/01/2013

Status: None

Materials/Assemblies	Amount	Unit	Distribution	SD^2 or 2*S	Min	Max	Comment
Aluminium, production mix, cast alloy, at plant/RER U	7.5	kg	Undefined				housing
Steel, converter, chromium steel 18/8, at plant/RER U	4	kg	Undefined				
Polyethylene terephthalate, granulate, bottle grade, at plant/RER U	3	kg	Undefined				used PET because PBT unavailable - assumed similar
Synthetic rubber, at plant/RER U	0.1	kg	Undefined				
Glass tube, borosilicate, at plant/DE U	1	kg	Undefined				glassware, condenser
Electronics for control units/RER U	0.5	kg	Undefined				estimate
Electronic component, unspecified, at plant/GLO U	0	kg	Undefined				NO LONGER USED (Components - previously 0.2kg)
Copper wire, technology mix, consumption mix, at plant, cross section 1 mm² EU-15 S	0.15	kg	Undefined				Electric motor windings

Appendix E.5.3. VACUUM PUMP

Vacuum Pump				
http://www.prestvacuo.com.br/pdf/C04_E-POD.pdf				

Name: Furnace 1100C_2013 | Image | Comment: Data based, on technical data sheet and discussion with managing director of EF furnaces 20/1/12. Total mass 22kg **new/amended datasets

Status: None

Materials/Assemblies	Amount	Unit	Distribution	SD^2 or 2*S	Min	Max	Comment
Steel, converter, unalloyed, at plant/RER U	0	kg	Undefined				
Galvanized steel sheet, at plant/RNA	11	kg	Undefined				based on casing dimensions given
Rock wool, at plant/CH U	6	kg	Undefined				estimate
Nickel, 99.5%, at plant/GLO U	1.5	kg	Undefined				estimate
Electronics for control units/RER S	0.5	kg	Undefined				estimate
Electronic component, unspecified, at plant/GLO U	0	kg	Undefined				**NO LONGER USED (previously 0.2kg)
Alkyd paint, white, 60% in H2O, at plant/RER U	0.25	kg	Undefined				estimate - powder coated paint unavailable
Synthetic rubber, at plant/RER U	0.25	kg	Undefined				estimate- feet, seals etc.
Sanitary ceramics, at regional storage/CH U	2.5	kg	Undefined				walls of furnace-only ceramic dataset available

Appendix E.5.5. SONICATOR

Name: Sonicator | Image | Comment: Total weight 1.4kg for 0.5litre unit

Status: None

Materials/Assemblies	Amount	Unit	[S!N	Comment
Chromium steel 18/8, at plant/RER U	1.15	kg		casing and surfaces
Controller _ Furnace Large Controller_2013	0.1	p		**new 07/01/2013
Ferrite, at plant/GLO U	0.1	kg		high fequency sonicator 'horn'
Copper wire, technology mix, consumption mix, at plant, cross section 1 mm² EU-15 S	0.05	kg		high fequency sonicator 'horn'
(Insert line here)				

APPENDIX F: SILICA DATASET

The substrate material used in the deposition of the iron and iron-palladium catalysts, are 'off-the shelf' chromatography grade precipitated silica. Precipitated silica has a microporous structure, with a large internal surface areas in excess of 700 m^2/g (Flörke *et al.* 2000) allowing high volumes of gas transfer to occur, whilst providing an inert support for the active catalyst materials.

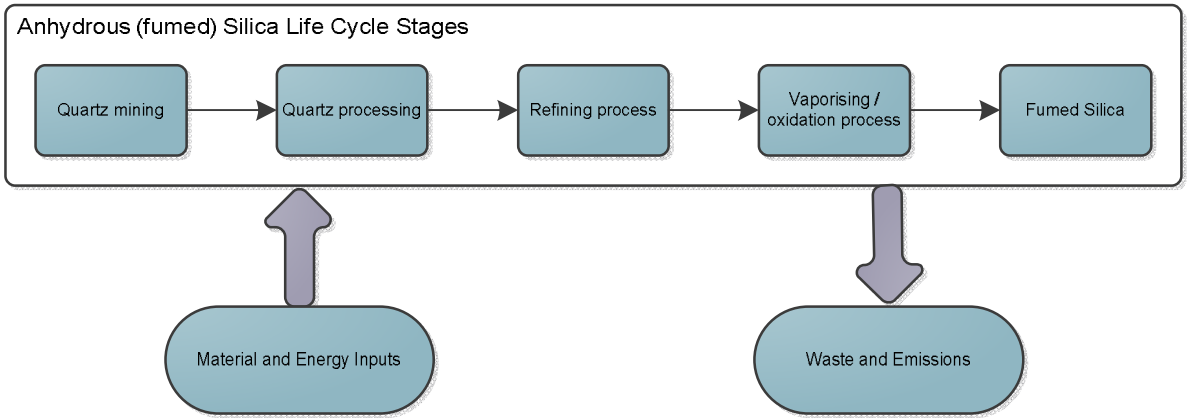


Figure F-5 Industrial route of anhydrous/Fumed/Amorphous silica production

Silica comes in many forms, from large quartz crystals to the synthetic amorphous powders (Flörke *et al.* 2000). Life cycle inventory datasets, available at the time of writing this thesis, are not comprehensive in their account of silica materials. A substantial amount of silica used is naturally found as natural sand, with such an important and widespread use in construction silica-sand dominates life cycle inventories. However, relatively few post-processing activities are conducted before the use of this material. Precipitated silica was found to be formed has been modelled as:

The most reported route for precipitated amorphous silica is through the acid neutralisation of alkali metal silicates (Flörke *et al.* 2000; National Center for Biotechnology Information 2011b):

$$Na_2O{\cdot}3.3SiO_2 + H_2SO_4 \rightarrow \mathbf{3.3SiO_2} + Na_2SO_4 + H_2O$$

It was deemed that this capture of silica life cycle impacts, the major input datasets are shown in would be of sufficient detail given the scope and depth of this work. The

Table F-7 Material input and plant infrastructure contributions in the production of 2 grams of amorphous (fumed) silica precipitate.

Dataset	Quantity	Unit
Sodium silicate, furnace process, pieces, at plant/ RER U	**4.063**	**g**
Sulphuric acid, liquid, at plant/RER U	**3.265**	**g**
Silicone plant/RER/I U	**4×10^{-10} * 2×10^{-3} = 8×10^{-13}**	**parts**

This silicone plant was used as a representative model dataset for the filtration, purification processing steps required in amorphous silica production.

APPENDIX G: SUPPORTING INFORMATION FOR ELECTROCHEMICAL PROCESS

Appendix G.1 PRECURSOR CHEMICAL AND NANOPARTICLE SOLUTION SYNTHESIS

Appendix G.1.1. GOLD NANOPARTICLE FORMATION:

To produce 20 nm particles of gold:

- 190ml of gold chloride (Chloroauric Acid), concentration of 0.25 mM solution.
- Stirred and heated at 115 C, for 1 hour. With addition of 10 ml of trisodium citrate, 1% solution.

Appendix G.1.2. PREPARATION OF PD SHELLS ON THE AU CORES – PART A

1.5 hours of – stirring, cold, of following reactants to form respective catalyst:

	Au NP solution (2.5 x 10-4 M)	Ascorbic Acid (0.1 M)	H2PdCl4 (1 mM)	Experimental Pd Shell
CS1 (Pd28)	50 mL	6 mL	6.6 mL	1.3 nm
CS10 (Pd82)	50 mL	6 mL	105 mL	9.9 nm

H_2PdCl_4: Na_2PdCl_4 with HCl

Appendix G.1.3. ADDITION OF CARBÓN BLACK – PART B

48 h stirring the necessary amount of carbon (vulcan) in the correct amount of NP soultion:

	Vulcan	NP solution	Experimental Weight %
CS1 (Pd28)	80 mg	430 mL	21.1
CS10 (Pd82)	80 mg	265 mL	20.2

Appendix G.1.4. INK FORMATION – PART C

Inks were made from the carbon-supported particles (2.0 mg) with Nafion (10% aqueous dispersion, 15 µL) and water (0.5 mL)

Appendix G.1.5. ELECTRODE COATING DEPOSITION – PART D

10 µl of the formed ink dropped onto tip of glassy carbon electrode and allowed to dry

Appendix G.2 CONSTITUENT CHEMICALS – STOICHIOMETRIC CALCULATIONS FOR INVENTORY REPORTING

		Mw (g/mol)	Moles	Mass (g)
Sodium tetrachloropalladate	Na2PdCl4	294.22	1	
	PdCl2		1	
>	Pd	106.42	1	
>	2HCl	72.92	1	
>	2NaCl	116.88	1	
		Mw (g/mol)	Moles	Mass (g)
dihydrogentetrachloropalladate (ii)	H2PdCl4	250.25	1.00E-03	0.25025
	Pd	106.42	1.00E-03	0.10642
	2HCl	72.92	1.00E-03	0.07292
	2NaCl	116.88	1.00E-03	0.11688
	2Na-	-45.97953856	1.00E-03	-0.045979539
		250.24	1.00E-03	0.25
		Mw (g/mol)	**Moles**	**Mass (g)**
Ascorbic Acid		176.12	0.1	17.612
Concentration, i.e. moles / litre				
	>		ml	
			6	0.105672
		Mw (g/mol)	Moles	Mass (g)
Chloroauric Acid	HAuCl4	339.785	2.50E-04	0.08494625
	Au	196.97	2.50E-04	4.92E-02
	1.5Cl2	106.38	2.50E-04	2.66E-02
	HCl	36.46	2.50E-04	9.12E-03
	>			
Both catalysts synthesis:				
		ml	g	mg
Chloroauric Acid		50	4.25E-03	4.247
Gold alone		50	2.46E-03	2.462
Catalyst		Quantity needed (ml)	Mass (g)	mg
CS1 (Pd28)	H2PdCl4	6.6	1.65E-03	1.652
	Pd	6.6	7.02E-04	0.702
CS10 (Pd82)	H2PdCl4	105	0.026	26.276
	Pd	105	0.011	11.174

Appendix G.3 DRY MASSES OF ELECTRODE COATING MATERIALS, AT EACH STAGE OF SYNTHESIS

Part A		**Gold**	**Palladium**			**Total dry weight**
CS1		2.462	0.702			3.164
CS10		2.462	11.174			13.636
Part B	**From A**	**Gold**		**Carbon black**		
CS1	687%	16.912	4.825	80		101.737
CS10	165%	4.050	18.381	80		102.432
Part C	**From B**	**Gold**	**Palladium**		Mass	
CS1	1.97%	**0.332**	**0.0948**		2	
CS10	1.95%	**0.079**	**0.359**		2	
Part C - continued			Nafion	Water	NP Vol	Total Vol
CS1			1.50E-05	5.00E-04	2.00E-06	5.17E-04
CS10			1.50E-05	5.00E-04	2.00E-06	5.17E-04
Part D	**From C**	Gold	Palladium	Vulcan	INK	
CS1	1.9%	6.4E-03	1.8E-03	3.9E-02	1.00E-05	
		14%	4%	82%		
CS10	1.9%	1.5E-03	6.9E-03	3.9E-02	1.00E-05	
		3%	15%	82%		

Appendix G.4 INVENTORY DATA FOR CHEMICALS USED

Appendix G.4.1. CHLOROAURIC ACID

Known outputs to technosphere. Products and co-products

Name	Amount	Unit	Quantity	Allocation	Waste type	Category	Comment
Chloroauric Acid - more	339.785	kg	Mass	100 %	not defined	Che...\Acids (inorganic)	
(Insert line here)							

Known outputs to technosphere. Avoided products

Name	Amount	Unit	Distribution	SD^2 or 2* Min	Max	Comment
(Insert line here)						

Inputs

Known inputs from nature (resources)

Name	Sub-compartmer	Amount	Unit	Distribution	SD^2 or 2* Min	Max	Comment
(Insert line here)							

Known inputs from technosphere (materials/fuels)

Name	Amount	Unit	Distribution	SD^2 or 2* Min	Max	Comment
Nitric acid, 50% in H2O, at plant/RER S	63.01*7/5 = 88.2	kg				Calc made based on 70% concentration. Therefore mass = 7/5 times as much...
Hydrochloric acid, from Mannheim process, at plant/RER S	145.84	kg	Undefined			
Gold, at regional storage/RER S	196.97	kg	Undefined			
Transport, lorry >16t, fleet average/RER U	0.39348*339.785 = 134	tkm				ECOINVENT VALUES
Transport, freight, rail/RER U	0.85714*339.785 = 291	tkm				ECOINVENT VALUES
Chemical plant, organics/RER/I U	4E-10*339.785 = 1.36E-7	p				ECOINVENT VALUES

Appendix G.4.2. GOLD NANOPARTICLE FORMATION

Name: Gold NP Formation - STOICH

Image

Comment: updated quantity of trisodium citrate to 1%

Status: None

Materials/Assemblies	Amount	Unit	[S!]	Comment
Chloroauric Acid	8.57E-5*200 = 0.0171	g		g/ml at the 2.5E-4 Mol concentration x (200 ml)
Trisodium Citrate	10*0.01 = 0.1	g		1% solution (therefore 10ml of water required (below))
Water, deionised, at plant/CH U	10+190 = 200	g		
Mech_Stirrer	1/(15*8760) = 7.61E-6	p		Updated from Infrastructure modelling xls
(Insert line here)				

Processes	Amount	Unit	Distribution	SD^2 or 2* Min	Max	Comment
Electricity mix/GB U	0.3	kWh	Undefined			
(Insert line here)						

Appendix G.4.3. DIHYDROGENTETRACHLOROPALLADATE

Known outputs to technosphere. Products and co-products

Name	Amount	Unit	Quantity	Allocation	Waste type	Category	Comment
Dihydrogentetrachloropalladate	250.25/1.581 = 158	kg	Mass	100 %	not defined	Chemicals\Inorganic	DILUTION ADJUSTMENT RATIO... based off ratio between pure substance and that containing non-used materials
(Insert line here)							

Known outputs to technosphere. Avoided products

Name	Amount	Unit	Distribution	SD^2 or 2* Min	Max	Comment
(Insert line here)						

Inputs

Known inputs from nature (resources)

Name	Sub-compartmer	Amount	Unit	Distribution	SD^2 or 2* Min	Max	Comment
(Insert line here)							

Known inputs from technosphere (materials/fuels)

Name	Amount	Unit	Distribution	SD^2 or 2* Min	Max	Comment
Palladium, at regional storage/RER U _Recycling Increased ~26% (Current)	106.42	kg	Undefined			
Hydrochloric acid, from Mannheim process, at plant/RER U	109.38	kg	Undefined			
Sodium chloride, powder, at plant/RER U	116.88	kg	Undefined			
Nitric acid, 50% in H2O, at plant/RER U	63.01	kg	Undefined			

Appendix G.4.4. AQUA REGIA

Known outputs to technosphere. Products and co-products

Name	Amount	Unit	Quantity	Allocation	Waste type	Category	Comment
Aqua Regia	88.2+109 = 197	g	Mass	100 %	not defined	Che...\Acids (inorganic)	3:1 ratio HCL to HNO3
(Insert line here)							

Known outputs to technosphere. Avoided products

Name	Amount	Unit	Distribution	SD^2 or 2* Min	Max	Comment
(Insert line here)						

Inputs

Known inputs from nature (resources)

Name	Sub-compartmer	Amount	Unit	Distribution	SD^2 or 2* Min	Max	Comment
(Insert line here)							

Known inputs from technosphere (materials/fuels)

Name	Amount	Unit	Distribution	SD^2 or 2* Min	Max	Comment
Hydrochloric acid, from Mannheim process, at plant/RER S	36.46094*3 = 109	g				
Nitric acid, 50% in H2O, at plant/RER S	63.01*7/5 = 88.2	g				Calc made based on 70% concentration. Therefore mass = 7/5 times as much...
(Insert line here)						

Appendix G.5 INVENTORY DATA FOR POTENTIOSTAT

Inventory data modelled on (Rowe *et al.* 2011)

Name: Potentiostat | Image | Comment: http://web.chem.ucsb.edu/~kwp/cheapstat/

Status: None

Materials/Assemblies	Amount	Unit	Comment
Integrated circuit, IC, logic type, at plant/GLO U	227	mg	Micro controller unit (IC chip)
Integrated circuit, IC, memory type, at plant/GLO U	680-227 = 453	mg	Amplifier (IC Chip) Analogue Switch (IC Chip) USB Interface (IC Chip) Voltage regulator (IC chip)
Capacitor, SMD type, surface-mounting, at plant/GLO U	234	mg	
Resistor, metal film type, through-hole mounting, at plant/GLO U	11	mg	
LCD glass, at plant/GLO U	1500	mg	
Panel components, at plant/GLO U	1500	mg	
Switch, toggle type, at plant/GLO U	1	g	
Plugs, inlet and outlet, for computer cable, at plant/GLO U	1	p	
Printed wiring board, surface mount, lead-free surface, at plant/GLO U	0.05*0.025 = 0.00125	m2	
Printed wiring board, through-hole, at plant/GLO U	0.05*0.025 = 0.00125	m2	
Glass fibre reinforced plastic, polyamide, injection moulding, at plant/RER U	2000	mg	
Power supply unit, at plant/CN U	0.1	p	approx tenth power requirement of PC
(Insert line here)			

Processes	Amount	Unit	Distribution	SD^2 or 2* Min	Max	Comment
(Insert line here)						

Appendix G.5.1. CIRCUIT BOARD FOR THE POTENTIOSTAT –

Source data of electronic components (Rowe et al. 2011)

Quantity	Component Identifier						Component Description	Material	Mass (mg)	Total mass (x quantity) [mg]	Length	W	Thickness	Vol	Density
							Control Circuit								
1	ATXMEGA32A4-AU	5.22	5.22	Mouser	MCU	TQFP-44	Micro controller unit (IC chip)	Y	227	227	10	10	1.2	120	
1	TLC2264ID	2.01	2.01	Mouser	Quad Op Amp	SOIC-14	Amplifier (IC Chip)	Y	122	122	9	6	1.2	64.8	1.89
1	DG612AEY-T1-E3	0.8	0.8	Mouser	Quad SPST Switch (4 NO)	SOIC-16 narrow	Analogue Switch (IC Chip)	Y	50	50	4.4	5	1.2	26.4	
1	FT232RL	4.5	4.5	Mouser	USB-UART	SSOP-28	USB Interface (IC Chip)	Y	263	263	10.2	7.8	1.75	139.23	
1	FAN2501S33X_Q	0.28	0.28	Mouser	Linear Regulator	see datasheet	Voltage regulator (IC chip)	Y	18	18	3	2.5	1.3	9.75	
										680					
1	EADOGM163EEA	11.9	11.93	Mouser	16x3 Display	see datasheet	LCD/LED Display	LCI DATA		0					
1	SKQUAAA010	1.5	1.5	Mouser	4 direction switch	see datasheet	Physical electric switch	LCI DATA		0	resin, metal contacts				
1	154-15322-E	0.51	0.51	Mouser	USB Mini Type B connector	see datasheet	Female USB port	PLUG		0	thermoplastic, copper alloy, gold coating, tin, solder,				
											nickel, polymide				
2	C0805C103K1RAC7210	0.05	0.1	Mouser	103 (0.01uF)	805		Y	1	3	1	0.5	0.5	0.25	
1	C0805C563K5RACTU	0.1	0.1	Mouser	56nF	805		Y	11	11	2	1.2	0.9	2.16	
7	C0805C104M5UAC7210	0.02	0.14	Mouser	104 (0.1uF)	805	Multilayer Ceramic Chip Capacitors	Y	10	68	2	1.2	0.78	1.872	
3	C0805C105J4RAC7025	0.07	0.21	Mouser	105 (1uF)	805		Y	13	39	2	1.25	1	2.5	
4	GRM219R60J106KE19D	0.09	0.36	Mouser	10uF	805		Y	11	44	2	1.25	0.85	2.125	5.18
2	GLCR2012T100M-HC	0.21	0.42	Mouser	10uH	805		Y	16	32	1.25	2	1.25	3.125	
2	MCB0805F400PT-T	0.03	0.06	Mouser	Ferrite Bead	805	Multilayer Ferrite Chip Beads	Y	19	38	2	1.25	1.45	3.625	
										234					
12	22-28-5020	0.08	0.96	Mouser	PDI Header Pins + Cell	.1 pitch	Circuit board header			0		brass, tin, thermosplastic			
1	TNPW080533K0DEEA	0.1	0.1	Mouser	33kohm (0.5%, 1/8W)	805	Thin Film Flat Chip Resistors	Y	1	1					
2	TNPW080510K0DEEA	0.11	0.22	Mouser	10kohm (0.5%, 1/8W)	805	Thin Film Flat Chip Resistors	Y	2	4					
1	PFC-W0805LF-03-1653-B	0.7	0.7	Mouser	165kohm (0.1%,.1W)	805	Thin Film Resistors	Y	6	6	2	1.25	0.5	1.25	
										11					
2	ME-100	0.15	0.3	Mouser	jumper		Jumper	Y	50	100	5mm * 5 * 2.5				
											Glass-filled polyester thermoplastic, tin over nickel plated phosphor b				
1	PCB	16.9	16.9	4PCB	PCB Board			Y							
							Case								
1	1593YGY	5.35	5.35	Mouser	Case			ABS Plastic							
1	101-0110-EV	0.15	0.15	Mouser	12x12 mountain switch			Plastic							

Masses of similar components calculated off references with both dimensions and mass values

Components	**References**
Thin Film Flat Chip Resistors	http://www.vishay.com/docs/28758/tnpw_e3.pdf
Multilayer Ceramic Chip Capacitors	http://www.kemet.com/kemet/web/homepage/kechome.nsf/vapubfiles/KEM_C1002_X7R_SMD.pdf/$file/KEM_C1002_X7R_SMD.pdf
Jumper	http://html.alldatasheet.com/html-pdf/335119/ARIES/ME-100/149/1/ME-100.html
Thin film resistor	http://www.irctt.com/pdf_files/PFC-COM.pdf
Analogue IC switch	http://www.vishay.com/docs/69904/dg611a.pdf
USB port	http://www.mouser.com/catalog/specsheets/KC-301259.pdf
PCB Header	http://www.molex.com/webdocs/datasheets/pdf/en-us/0022285020_PCB_HEADERS.pdf

Appendix G.6 ACID QUANTITY REQUIRED FOR METAL DISSOLUTION

	Pure Metal Mass (g)			Moles				Aqua Regia for dissolution				Mass	Volume
	Au	Pd	Pt	Au	Pd	Pt		Au	Pd	Pt	Total		
CS1	6.43E-06	1.83E-06		3.27E-08	1.72E-08			1.31E-07	1.03E-07		2.34E-07	4.04E-05	2.70E-05
CS10	1.53E-06	6.94E-06		7.78E-09	6.52E-08			3.11E-08	3.91E-07		4.23E-07	7.28E-05	4.87E-05
Counter Pt			2.42E-05			1.24E-07				2.48E-07	2.48E-07	4.27E-05	2.86E-05
Counter Pt _ lean			3.63E-06			1.86E-08				3.72E-08	3.72E-08	6.41E-06	4.29E-06

				Molar Relationships (req for 1 mol dissolution of pure metal)			
Aqua Regia	Mw (g/mol)	density (g/ml)		Au	Pd	Pt	
(3:1) HCL:HNO3	172.4	1.495		4	2	6	

APPENDIX H: NATURAL DERIVED ACID MODELLING IN LCA

Citric acid is a precursor in the formation of the gold nanoparticles of chapter 7. Additionally ascorbic acid is used during the stage of coating the gold nanoparticles with palladium.

Citric acid is typically produced via a biological / fermentation based processes (Lopez-Garcia 2000); however comprehensive inventory accounts the production route were missing from accessible datasets. It was therefore necessary to use proxy datasets when measuring the impacts of these inputs. The BREW Project (Patel *et al.* 2006) covers bulk bio-chemical production of both ethanol and citric acid, both of which are founded on established fermentation processes (albeit ethanol anaerobic and citric acid aerobic). A great deal of similarities is shared between ethanol and citric acid processing stages, for example:

- same supply of glucose, water, nutrients and heated air (35 °C) feeds,
- processes all occur under ambient pressures, and
- similar vessel temperatures across like for like stages, for example: fermentation stage at 30 °C, distillation of product ~ 80 °C.

It was therefore assumed that the use of an ethanol cradle-to-factory gate dataset could be broadly transferable for the purpose of this assessment. In ecoinvent V2.2 (Ecoinvent Database v2.2 2010) 25 datasets pertaining to ethanol fermentation processes via different feedstocks are provided. The choice of process is subject to a great deal of uncertainty since the glucose source is founded in crops, and the choice of feedstock is thus dependent on geographical and economic drivers. Common citric acid feedstocks are: sugarcane molasses, sugarcane, and sugar beets (Lopez-Garcia 2000), the corresponding ethanol datasets were chosen to represent this. In order to prevent discrepancies between the results, ascorbic acid was modelled identical to citric acid. Adjustments were made to the ethanol datasets, however, to accommodate the changes in average yield from the process, ethanol being 46 % (Patel *et al.* 2006), and the aerobic acids appreciably more for the same quantity of feedstock:

- Citric Acid, biological yield of 86% (Lopez-Garcia 2000; Patel *et al.* 2006)

- Ascorbic acid, biological yield of 50% (Bremus *et al.* 2006; Patel *et al.* 2006)

Sugarcane / sugar beet ~ 20-30% sucrose; sucrose constitutes approximately 52% glucose by molecular weight, the necessary precursor for ethanol fermentation. This is represented in the Ecoinvent datasets for the mass of plant feedstocks used toward pure ethanol extraction.

Appendix H.1 CITRIC ACID

Known outputs to technosphere. Products and co-products

Name	Amount	Unit	Quantity	Allocation	Waste type	Category	Comment
Citric Acid - based on ethanol	1.87	kg	Mass	100 %	not defined	Chemi...\Acids (organic)	Feedstock yield of ethanol = 0.46, citric acid = 0.86
(Insert line here)							

Known outputs to technosphere. Avoided products

Name	Amount	Unit	Distribution	SD^2 or 2* Min	Max	Comment
(Insert line here)						

Inputs

Known inputs from nature (resources)

Name	Sub-compartmer	Amount	Unit	Distribution	SD^2 or 2* Min	Max	Comment
(Insert line here)							

Known inputs from technosphere (materials/fuels)

Name	Amount	Unit	Distribution	SD^2 or 2* Min	Max	Comment
Ethanol, 95% in H2O, from sugarcane molasses, at sugar refinery/BR S	0.333	kg	Undefined			
Ethanol, 95% in H2O, from sugar cane, at fermentation plant/BR S	0.334	kg	Undefined			
Ethanol, 95% in H2O, from sugar beets, at fermentation plant/CH S	0.333	kg	Undefined			

Appendix H.2 ASCORBIC ACID

Known outputs to technosphere. Products and co-products

Name	Amount	Unit	Quantity	Allocation	Waste type	Category	Comment
Ascorbic Acid - based on ethanol	0.5/0.46 = 1.09	kg	Mass	100 %	not defined	Chemi...\Acids (organic)	Feedstock yield of ethanol = 0.46, ascorbic acid = 0.5
(Insert line here)							

Known outputs to technosphere. Avoided products

Name	Amount	Unit	Distribution	SD^2 or 2* Min	Max	Comment
(Insert line here)						

Inputs

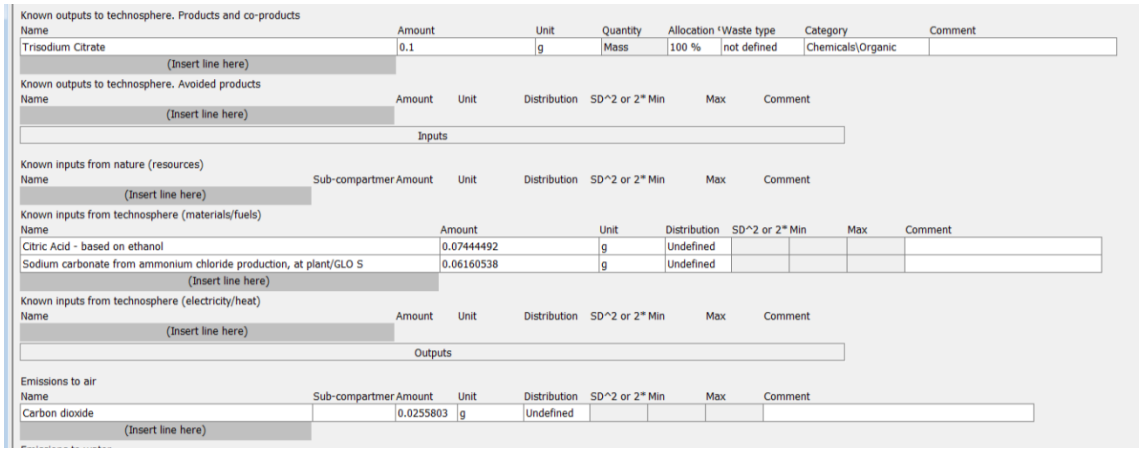
Known inputs from nature (resources)

Name	Sub-compartmer	Amount	Unit	Distribution	SD^2 or 2* Min	Max	Comment
(Insert line here)							

Known inputs from technosphere (materials/fuels)

Name	Amount	Unit	Distribution	SD^2 or 2* Min	Max	Comment
Ethanol, 95% in H2O, from sugarcane molasses, at sugar refinery/BR S	0.333	kg	Undefined			
Ethanol, 95% in H2O, from sugar cane, at fermentation plant/BR S	0.334	kg	Undefined			
Ethanol, 95% in H2O, from sugar beets, at fermentation plant/CH S	0.333	kg	Undefined			
(Insert line here)						

Appendix H.3 TRISODIUM CITRATE



Known outputs to technosphere. Products and co-products

Name	Amount	Unit	Quantity	Allocation %	Waste type	Category	Comment
Trisodium Citrate	0.1	g	Mass	100 %	not defined	Chemicals\Organic	
(Insert line here)							

Known outputs to technosphere. Avoided products

Name	Amount	Unit	Distribution	SD^2 or 2* Min	Max	Comment
(Insert line here)						

Inputs

Known inputs from nature (resources)

Name	Sub-compartmer	Amount	Unit	Distribution	SD^2 or 2* Min	Max	Comment
(Insert line here)							

Known inputs from technosphere (materials/fuels)

Name	Amount	Unit	Distribution	SD^2 or 2* Min	Max	Comment
Citric Acid - based on ethanol	0.07444492	g	Undefined			
Sodium carbonate from ammonium chloride production, at plant/GLO S	0.06160538	g	Undefined			
(Insert line here)						

Known inputs from technosphere (electricity/heat)

Name	Amount	Unit	Distribution	SD^2 or 2* Min	Max	Comment
(Insert line here)						

Outputs

Emissions to air

Name	Sub-compartmer	Amount	Unit	Distribution	SD^2 or 2* Min	Max	Comment
Carbon dioxide		0.0255803	g	Undefined			
(Insert line here)							

Cordes, H. (1965). US 3217022: Production of ferrocene compounds. U. S. P. Office. USA: 8.

National Center for Biotechnology Information (2011). PubChem Compound Database; CID=7611. Ferrocene.

Oxford, U. o. (1996). "Ferrocene - Synthesis." Retrieved February 2012, 2012, from http://www.chem.ox.ac.uk/mom/ferrocene/synthesis.html.

APPENDIX I: JOURNAL PUBLICATIONS

Contribution:

- Lead author of "Identifying the largest environmental life cycle impacts during carbon nanotube synthesis via chemical vapour deposition." Journal of Cleaner Production (Griffiths *et al.* 2013a)
- Joint lead author "Using Life Cycle Assessment to Measure the Environmental Performance of Catalysts and Directing Research in the Conversion of CO_2 into Commodity Chemicals: a look at the potential for fuels from 'thin-air'." RSC Advances.(Griffiths *et al.* 2013b)
- Co-author "Use of LCA as a development tool within early research: challenges and issues across different sectors." The International Journal of Life Cycle Assessment(Hetherington *et al.* 2013)